

For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAE NSIS



Regulations Regarding Theses and Dissertations

[illegible]

THE UNIVERSITY OF ALBERTA

"SULFUR DIOXIDE AND ITS EFFECT ON
DISPLACEMENT EFFICIENCY AND PERMEABILITY"

BY

HARRY E. RIPLEY



A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE IN PETROLEUM ENGINEERING

FACULTY OF ENGINEERING
DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

EDMONTON, ALBERTA

JULY, 1967

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Sulfur Dioxide and Its Effect on Displacement Efficiency and Permeability" submitted by Harry E. Ripley, B.Sc. Eng., in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Engineering.

ABSTRACT

A series of tests were conducted using sulfur dioxide-water solutions to observe their effect on the displacement efficiency of oil from a porous system. Distilled water, liquid sulfur dioxide, diesel fuel, Swan Hills crude oil, Turner Valley crude oil, limestone core from Swan Hills and alundum core were used.

Solutions of sulfur dioxide slightly increased oil recovery over conventional water flooding. This increase in oil recovery is attributed to a decrease in oil viscosity and interfacial tension between oil and water.

A significant increase in permeability was noted when flowing sulfur dioxide solutions through limestone core. This increase was caused by a chemical reaction of the acidic solution with the limestone.

ACKNOWLEDGEMENTS

The writer wishes to express sincere appreciation to the following:

Dr. D. L. Flock for his guidance and constructive advice throughout this project,

The members of the Department Technical Staff for their assistance and advice in the design and construction of equipment,

Mr. M. R. Wallace for reviewing the manuscript,

Halliburton Oil Well Cementing Co. Ltd. for assistance and advice,

Edna, my wife, for her typing, drafting and most important her encouragement.

The financial assistance of the University of Alberta and the Research Council is gratefully acknowledged.

TABLE OF CONTENTS

	<u>PAGE NO.</u>
ABSTRACT	a
ACKNOWLEDGEMENTS	b
LIST OF TABLES	i
LIST OF FIGURES	iii
REVIEW OF LITERATURE	
Physical Properties of Sulfur Dioxide	5
Sulfur Dioxide and Oil	5
Solubility of Sulfur Dioxide in Water	5
Sulfur Dioxide and Calcium Carbonate	9
Earlier Work	11
EXPERIMENTAL APPARATUS AND PROCEDURE	
Mixing Solutions	14
Change in Permeability	15
Recovery	19
Reaction Rate	22
DISCUSSION OF RESULTS	
Change in Permeability	23
Recovery	26
Reaction Rate	35
CONCLUSIONS	41

TABLE OF CONTENTS - Continued

	<u>PAGE NO.</u>
RECOMMENDATIONS	43
NOMENCLATURE	44
BIBLIOGRAPHY	46
APPENDIX	48
1. Introduction	49
2. Objectives	50
3. Scope	51
4. Methodology	52
5. Results and Discussion	53
6. Conclusions	54
7. Recommendations	55
8. References	56
9. Appendix	57
10. Glossary	58
11. Bibliography	59
12. Index	60
13. List of Figures	61
14. List of Tables	62
15. Acknowledgments	63
16. Appendix	64
17. Glossary	65
18. Bibliography	66
19. Index	67
20. List of Figures	68
21. List of Tables	69
22. Acknowledgments	70
23. Appendix	71
24. Glossary	72
25. Bibliography	73
26. Index	74
27. List of Figures	75
28. List of Tables	76
29. Acknowledgments	77
30. Appendix	78
31. Glossary	79
32. Bibliography	80
33. Index	81
34. List of Figures	82
35. List of Tables	83
36. Acknowledgments	84
37. Appendix	85
38. Glossary	86
39. Bibliography	87
40. Index	88
41. List of Figures	89
42. List of Tables	90
43. Acknowledgments	91
44. Appendix	92
45. Glossary	93
46. Bibliography	94
47. Index	95
48. List of Figures	96
49. List of Tables	97
50. Acknowledgments	98
51. Appendix	99
52. Glossary	100
53. Bibliography	101
54. Index	102
55. List of Figures	103
56. List of Tables	104
57. Acknowledgments	105
58. Appendix	106
59. Glossary	107
60. Bibliography	108
61. Index	109
62. List of Figures	110
63. List of Tables	111
64. Acknowledgments	112
65. Appendix	113
66. Glossary	114
67. Bibliography	115
68. Index	116
69. List of Figures	117
70. List of Tables	118
71. Acknowledgments	119
72. Appendix	120
73. Glossary	121
74. Bibliography	122
75. Index	123
76. List of Figures	124
77. List of Tables	125
78. Acknowledgments	126
79. Appendix	127
80. Glossary	128
81. Bibliography	129
82. Index	130
83. List of Figures	131
84. List of Tables	132
85. Acknowledgments	133
86. Appendix	134
87. Glossary	135
88. Bibliography	136
89. Index	137
90. List of Figures	138
91. List of Tables	139
92. Acknowledgments	140
93. Appendix	141
94. Glossary	142
95. Bibliography	143
96. Index	144
97. List of Figures	145
98. List of Tables	146
99. Acknowledgments	147
100. Appendix	148
101. Glossary	149
102. Bibliography	150
103. Index	151
104. List of Figures	152
105. List of Tables	153
106. Acknowledgments	154
107. Appendix	155
108. Glossary	156
109. Bibliography	157
110. Index	158
111. List of Figures	159
112. List of Tables	160
113. Acknowledgments	161
114. Appendix	162
115. Glossary	163
116. Bibliography	164
117. Index	165
118. List of Figures	166
119. List of Tables	167
120. Acknowledgments	168
121. Appendix	169
122. Glossary	170
123. Bibliography	171
124. Index	172
125. List of Figures	173
126. List of Tables	174
127. Acknowledgments	175
128. Appendix	176
129. Glossary	177
130. Bibliography	178
131. Index	179
132. List of Figures	180
133. List of Tables	181
134. Acknowledgments	182
135. Appendix	183
136. Glossary	184
137. Bibliography	185
138. Index	186
139. List of Figures	187
140. List of Tables	188
141. Acknowledgments	189
142. Appendix	190
143. Glossary	191
144. Bibliography	192
145. Index	193
146. List of Figures	194
147. List of Tables	195
148. Acknowledgments	196
149. Appendix	197
150. Glossary	198
151. Bibliography	199
152. Index	200

LIST OF TABLES

<u>TABLE</u>	<u>TITLE</u>	<u>PAGE NO.</u>
1	Values for Constants a and b as given by Wells and MacClaren (22).	A 1
2	Summary of Linear Flow Tests Observing Change in Permeability	A 3
3	Summary of Radial Flow Tests Observing Change in Permeability	A 4
4	Solubility of SO ₂ in Turner Valley Crude	A 5
5	Solubility of SO ₂ in Swan Hills Crude	A 6
6	Pressure-Volume Data for Core No. 4-L	A 7
7	Pressure-Volume Data for Core No. 6	A 8
8	Pressure-Volume Data for Core No. 13	A 11
9	Pressure-Volume Data for Core No. 14	A 12
10	Pressure-Volume Data for Core No. 16	A 13
11	Pressure-Volume Data for Core Nos. 4, 5 and 7	A 14
12	Displacement Test Recovery Data - Test No. 12	A 15
13	Displacement Test Recovery Data - Test No. 13	A 16
14	Displacement Test Recovery Data - Test No. 14	A 17
15	Displacement Test Recovery Data - Test No. 15	A 18
16	Displacement Test Recovery Data - Test No. 16	A 19
17	Displacement Test Recovery Data - Test No. 17	A 21
18	Reaction of Sulfur Dioxide Solutions on Limestone Chips	A 22

<u>TABLE</u>	<u>TITLE</u>	<u>PAGE NO.</u>
19	pH Versus Per Cent Sulfur Dioxide	A 23
20	Radial Flow Tests Observing Change in Permeability - Test No. 20	A 24
21	Radial Flow Tests Observing Change in Permeability - Test No. 21	A 25
22	Radial Flow Tests Observing Change in Permeability - Test No. 22	A 26
23	Radial Flow Tests Observing Change in Permeability - Test No. 23	A 27
24	Radial Flow Tests Observing Change in Permeability - Test No. 24	A 28
25	Radial Flow Tests Observing Change in Permeability - Test No. 25	A 29
	Sample Calculations	A 30

LIST OF FIGURES

<u>FIGURE</u>	<u>TITLE</u>	<u>PAGE NO.</u>
1	Gauge Pressure for Sulfur Dioxide-Water Solutions	7
2	Solubility of Sulfur Dioxide in Swan Hills and Turner Valley Crude Oil	12
3	Schematic Sketch of Flow Apparatus	18
4	Permeability Change During Linear Flow	24
5	Permeability Change During Linear Flow with a Sulfur Dioxide Concentration Parameter	25
6	Permeability Change During Radial Flow	27
7	Recovery of Diesel Fuel Displaced with Sulfur Dioxide Solutions	29
8	Recovery of Swan Hills Crude Displaced with Sulfur Dioxide Solutions from Alundum Core	31
9	Recovery of Swan Hills Crude Displaced with Sulfur Dioxide Solutions from "Oil-Wet" Alundum Core	33
10	Recovery of Turner Valley Crude Displaced with Sulfur Dioxide Solutions from "Oil-Wet" Alundum Core	34
11	pH of Sulfur Dioxide Solutions	36
12	Reaction of Sulfur Dioxide Solutions on Limestone Chips at 75°F	37
13	Reaction of Sulfur Dioxide Solutions on Limestone Chips at Various Temperatures	39
14	Reaction of Sulfur Dioxide Solutions on Limestone Chips at Various Pressures	40

INTRODUCTION

One phase of petroleum research currently receiving attention by the oil industry is the search for new methods for the improvement of oil recovery displacement efficiency by fluid injection^{(13)*}. Many important improvements that have been made to date might be considered mechanical in nature. Some of these are improved well completion methods, purification of injected water, the control of injection rate so that the most effective pressures and volumes are applied to the reservoir, and the adoption of uniform well spacing. To a large extent these improvements serve mainly to accelerate the recovery of oil but may not significantly reduce the residual oil saturation.

Residual oil saturation at time of abandonment is usually in the range of 30 to 50 per cent of the total reservoir pore volume even under the most favorable primary or secondary recovery mechanism. It has been calculated⁽¹³⁾ that a reduction of one per cent in the present recovery limit would increase the world's recoverable oil by more than one billion barrels.

*Numbers in brackets refer to references in Bibliography at end of text.

The injection of fluids into an oil reservoir to increase the rate of recovery has been used and its benefits realized almost since the discovery of oil in America⁽²⁰⁾. It is only since World War II, however, that fluid injection has been extensively used. The phenomenal growth in the amount of oil that is produced from fluid injection projects in the last few years is evidence of the significance and importance that this type of operation is to the oil industry today.

A method that has been developed and shown favorable results in accelerating the oil recovery and, possibly more important, has resulted in reduced residual oil saturations, uses carbonated water as the flood medium. Laboratory tests⁽¹¹⁾ using this process have been successful in reducing the oil saturation in homogeneous sands to a low range of five to eight per cent of the total pore volume. Recent work⁽⁵⁾ at the University of Alberta using high viscosity Lloydminster crude oil displaced by carbonated brine indicated a residual oil saturation of eighteen per cent. The residual oil saturation using non-carbonated brine and the same oil resulted in a residual oil saturation of 79.3 per cent.

The benefits realized by the use of carbonated water are believed principally due to chemical reaction between carbon dioxide and carbonic acid with hydrocarbon

compounds, rather than a thermodynamic process of the expansion of the carbon dioxide as it comes from solution⁽¹²⁾.

James W. Martin, the developer of the Orco Process, discovered that under certain conditions of pressure, temperature and crude oil composition, carbon dioxide will react with certain constituents of the crude producing unstable solvents or surface active compounds. Carbon dioxide is soluble both in crude oil and in water, therefore, it will penetrate to the rock surface of both hydrophobic and hydrophilic reservoirs.

Another feature of carbon dioxide is its effect on the solubility of gases in crude oil. For example, in Pennsylvania Grade crude oil at 900 psi, thirty volumes of methane will dissolve in one volume of oil. However, seventy volumes of a carbon dioxide methane mixture in the ratio of 1.54 to 1.0 could be dissolved in the oil at the same temperature and pressure⁽²¹⁾.

Considering the advantages that might be gained by the use of carbon dioxide and after considering the characteristics of carbon dioxide to those of sulfur dioxide, an investigation was conducted to determine if sulfur dioxide could be used to improve oil recovery. Preliminary work using slugs of pure liquid sulfur dioxide

as a flood fluid in carbonate rocks gave a variety of results and often the experiment terminated with the complete "plugging off" of the core. It was found that mixtures of sulfur dioxide and water gave promising results. Since this mixture is acidic and reacts with carbonate rock, the present work was conducted in two phases. Experimental work to determine the effect sulfur dioxide has on oil recovery was done using "non-reactive" alundum cores. The effect sulfur dioxide has on the permeability was determined using short limestone cores in the absence of any hydrocarbon. The effect of temperature, pressure and acid concentration on the reaction were also compared using limestone chips.

REVIEW OF LITERATURE

Physical Properties of Sulfur Dioxide

Sulfur dioxide at standard temperature and pressure is a colorless gas characterized by a sharp irritating odor⁽¹⁸⁾. When subjected to a pressure of one atmosphere it will liquify at -10.02°C . Sulfur dioxide gas will readily liquify at higher temperatures when subjected to slight compression. The vapor pressure at 100°F is only 84.5 psia⁽¹⁴⁾. Liquid sulfur dioxide is yellowish and translucent with a viscosity of 0.28 centipoise at 70°F ⁽⁴⁾.

Sulfur Dioxide and Oil

The Edeleanu process of liquid extraction in crude oil refining utilizes sulfur dioxide as the solvent⁽⁸⁾. In general, one volume of solvent is circulated per volume of charge stock. The solvent removes material of low hydrogen content, principally aromatics, from materials of higher hydrogen content. Sulfur dioxide has been used to extract petroleum stocks of all boiling ranges⁽⁸⁾.

Solubility of Sulfur Dioxide in Water

On a comparative basis sulfur dioxide is sixty times more soluble in water than carbon dioxide and also ionizes to a greater extent⁽³⁾. Most of the data in the literature pertaining to the solubility of sulfur dioxide in water is for a total pressure of one atmosphere^(9,10,15).

The maximum concentration at one atmosphere and at 72°F is 105.0 grams per litre of water which is seven per cent by volume. Campbell and Maass⁽¹⁾ give vapor pressures and conductivities of sulfur dioxide-water solutions over a temperature range of 23 to 135°C and various concentrations up to eight per cent by weight of sulfur dioxide. They also give the densities of the aqueous solutions up to fifteen per cent sulfur dioxide.

Sulfur dioxide and water are not miscible at all concentrations. The literature⁽²²⁾ cites that the concentration of sulfur dioxide in a saturated aqueous solution would vary from about twenty-six per cent at 25°C to thirty per cent at 65°C on a volume basis. Wells and MacClaren have determined the total pressure for sulfur dioxide-water solutions of various concentrations at various temperatures. A plot of their work is shown on Figure 1. The pressure of a saturated aqueous solution is only slightly less than the pressure of pure sulfur dioxide. An equation for the total system pressure has been proposed by Plummer⁽¹⁶⁾ and work of Wells and MacClaren⁽²²⁾ improved its validity over a wider range. The equation is:

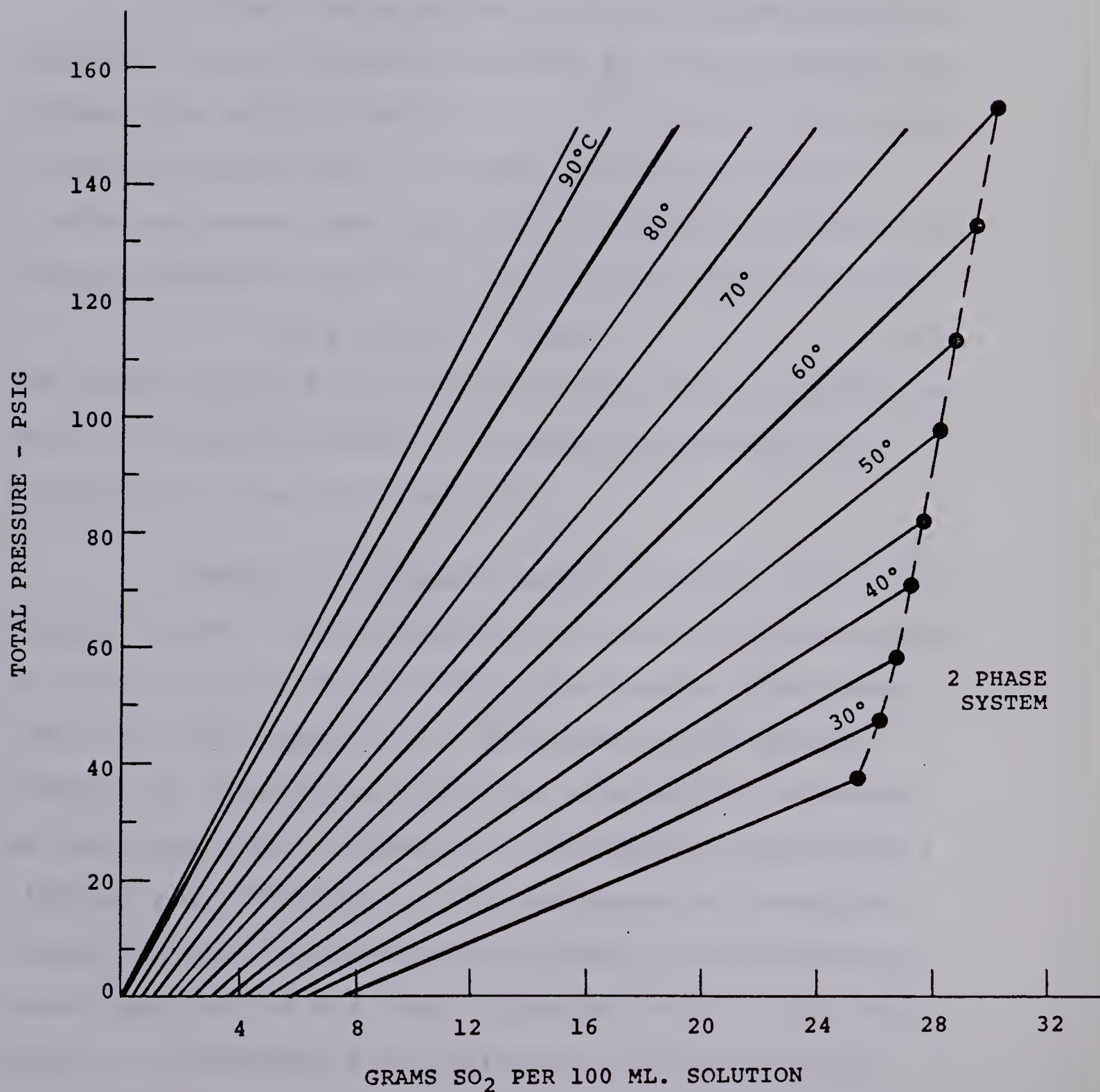
$$\text{Log } P_m = b \log P_w + a \quad (1)$$

Where:

P_m	=	total system pressure at $t^\circ\text{C}$
P_w	=	vapor pressure of water at $t^\circ\text{C}$
b	=	slope
a	=	intercept

FIGURE 1

GAUGE PRESSURE FOR SYSTEM
 $\text{SO}_2 - \text{H}_2\text{O}$
(AFTER WELLS & MACCLAREN ²²)



The values given by Wells and MacClaren for the constants "a" and "b" are found in Table 1. A variety of concentrations from dilute to pure sulfur dioxide were used for the experiments included in this report.

It has been experimentally determined by several methods⁽³⁾ that an aqueous solution of sulfur dioxide will contain free sulfur dioxide, i.e., it does not all combine to form sulfurous acid. The reaction between sulfur dioxide and water that does occur is usually considered to produce sulfurous acid⁽¹⁸⁾. The chemical equation being:

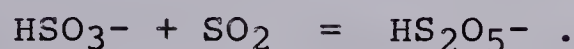
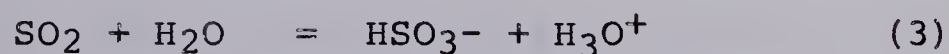


The extent to which the reaction takes place is controlled mainly by the concentration of sulfur dioxide and the temperature of the solution^(1,3).

Campbell and Maass⁽¹⁾ have determined the equilibrium constants for the reaction for several concentrations of sulfur dioxide at different temperatures. They have shown that the proportion of dissolved sulfur dioxide existing in solution as sulfurous acid rapidly decreased as the temperature increased. For example, considering a five per cent solution at 10°C the amount of uncombined sulfur dioxide in the solution amounted to approximately twenty per cent of the total dissolved while at 22°C the amount of uncombined sulfur dioxide was approximately fifty per cent of the total dissolved. Sulfurous acid is

often considered to be a weak acid but in effect it behaves as a strong acid, similar to the organic sulfonic group. Its apparent weakness is a result of the small amount of sulfurous acid actually present⁽¹⁾.

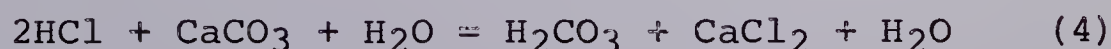
A recent investigation⁽²⁾ however indicates that there is no stable sulfurous acid formed in the reaction between sulfur dioxide and water. In concentrations of 0.1 to 1.0 molar, sulfur dioxide in water was found to be:



If this is true then the reaction between sulfur dioxide and water is not as simple as previously predicted and the ionization of sulfurous acid is almost complete.

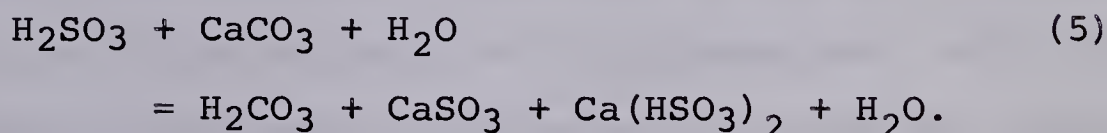
Sulfur Dioxide and Calcium Carbonate

Acidizing carbonate reservoirs has been practiced since the early stages of the petroleum industry. Since 1930⁽⁷⁾ the practice has become very common and although even today the procedure is often carried out by a rule of thumb method based on past experience, the reactions involved are better understood. One thing now certain is that the reaction between hydrochloric acid, the common oil-field acid, and limestone occurs within a few minutes. The reaction being:

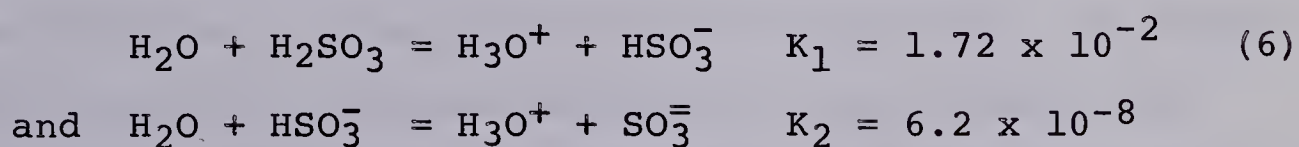


The carbon dioxide will remain in solution until the pressure is reduced below 1000 psi. The calcium chloride that is produced is readily soluble in the water solvent.

In the case of sulfurous acid and limestone the reaction is:



In this reaction, since sulfurous acid is diprotic, two series of salts could be formed, the normal sulfite, CaSO_3 and the bisulfite, $\text{Ca}(\text{HSO}_3)_2$. Calcium bisulfite is readily soluble in water, however, calcium sulfite is only slightly soluble⁽¹⁸⁾. The extent to which either of these salts will form depends in part upon the ionization of the sulfurous acid. The ionization of a diprotic acid in water proceeds in two steps and for sulfurous acid it is:



Where: K_1 = equilibrium constant for Step 1 at 25°C

K_2 = equilibrium constant for Step 2 at 25°C.

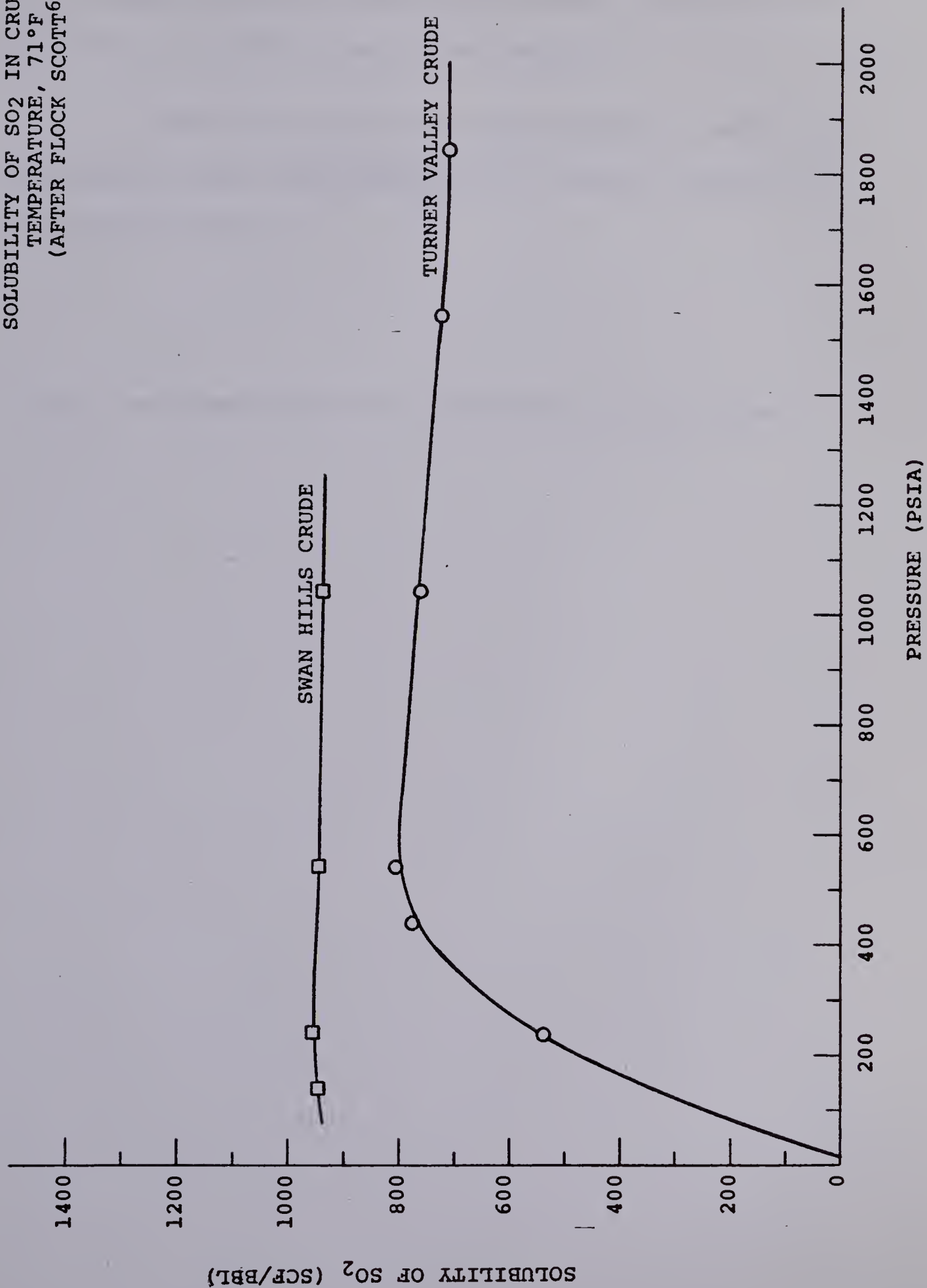
The second ionization, as shown by the respective equilibrium constant is small compared to the first ionization. Some writers⁽¹⁾ consider that the second ionization is so small that it may be safely neglected. In any case there will be a much larger amount of the bisulfite ion in the solution than sulfite. From this it may be concluded that the bisulfite salt will be the predominant salt with very little of the normal sulfite salt present and therefore, the solubility of calcium sulfite will probably not affect the reaction. The experimental work conducted during this project neither supports nor discredits this conclusion.

Earlier Work

Prior work⁽⁶⁾ at the University of Alberta determined the solubility of sulfur dioxide in Swan Hills and Turner Valley crudes. This was done by mixing the two liquids in a liquid level gauge and allowing equilibrium to be attained at a given pressure and temperature. A sample of the crude oil was then extracted under isobaric and isothermal conditions. The pressure of the sample was then reduced to atmospheric and the sulfur dioxide gas that was released was measured in a gas burette. The volume of the crude oil remaining was then measured. Data from this work are shown in Tables 4 and 5, and Figure 2. It was found under the test conditions that the Turner Valley crude had a relatively constant solubility of 750 cubic feet of

FIGURE 2

SOLUBILITY OF SO₂ IN CRUDE OIL
TEMPERATURE, 71°F
(AFTER FLOCK SCOTT⁶)



sulfur dioxide per barrel and the solubility of the Swan Hills crude was also relatively constant, containing 950 cubic feet of sulfur dioxide per barrel.*

The solubility of sulfur dioxide in water as reported by Wells and MacClaren⁽²²⁾ is 26.2 per cent by volume at 80.6°F.

* Refer to Nomenclature for the definition of terms.

EXPERIMENTAL APPARATUS AND PROCEDURE

The work undertaken in this project was an attempt to establish whether sulfur dioxide might be used advantageously as a displacing fluid in secondary recovery operations.

Preliminary work using limestone cores and slugs of pure sulfur dioxide gave varying results and frequently the core "plugged off". Solutions of sulfur dioxide and water of various concentrations were then used under a variety of test conditions. Because of the reaction of the sulfur dioxide-water solution on limestone, the oil recovery portion of this work was conducted utilizing alundum cores. Limestone cores were used to examine the effect sulfur dioxide and water has on the rocks' permeability. Tests to determine the reaction time of sulfur dioxide-water solutions were conducted using limestone chips.

Mixing Solutions

A cylinder containing 150 pounds of liquid, commercial grade sulfur dioxide (99.9 per cent sulfur dioxide) was obtained from The Matheson Company. The cylinder was inverted and mounted in an elevated location so that sulfur dioxide could be obtained in a liquid phase.

The mixing of the sulfur dioxide-water solutions were conducted independently of the flow apparatus and the solutions were transferred via the mixing cylinder. A Hoke stainless steel high pressure cylinder having a capacity of 1300 cc was used as the mixing cylinder. The mixing cylinder was evacuated and the required volume of water introduced. A 200-cc capacity Ruska positive displacement pump calibrated to 0.2 cc was used to transfer the liquid sulfur dioxide from the supply cylinder to the mixing cylinder. The two liquids were mixed by shaking the mixing cylinder by hand. Five different concentrations of sulfur dioxide were used during the experiments.

Change in Permeability

The permeability tests were conducted using both radial and linear flow through limestone cores. The limestone cores that were used for the tests were cut from regular four inch cores taken from the Swan Hills reef. The cores had been previously cleaned and extracted. The limestone cores used for linear flow were mounted in steel casing and the annular space filled with epoxy resin. A continuous impervious bond was thus formed between the core and the casing after the resin had cured. The ends of the core were cut flush with the ends of the casing. Grooved stainless steel end plates and neoprene gaskets were used to make a seal with the resin and to direct the fluid

against the entire core face. The two end plates were connected by tie bolts that were tightened sufficiently to ensure a fluid seal between the end plates and the core.

The radial test cores were mounted in a specially designed stainless steel core holder. This holder permitted the test fluids to be injected into a hole drilled through the centre of the core and the effluent to escape from the perimeter of the core. During the testing operations the cores were placed in a constant temperature air bath. The temperature was controlled using an Aminco micro relay and thermostat. The temperature was maintained within plus or minus one degree of the test temperature. The bulk volume of each core was determined by direct measurement. The pore volume of the cores used for radial flow was obtained using the Boyles Law Porosimeter.

The linear cores, which were mounted in casing, were evacuated at the downstream manifold until the pressure at the upstream was four centimeters of mercury or less. The core was then saturated with distilled water. The porosity of each core was determined by calibrating the quantity of water absorbed⁽¹⁷⁾ and checked by the method of weight difference. After the porosity had been determined, distilled water was injected at a constant rate holding a back pressure of 70 psi until the differential pressure stabilized. This usually occurred by the time two or three

pore volumes of water had been pumped. The permeability was then calculated. The core was left saturated for at least twelve hours and the permeability was again checked. There was never a significant change in pressure differential indicating the cores did not contain any hydratable minerals.

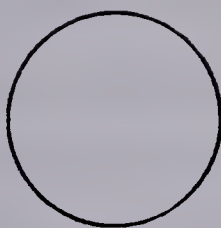
The sulfur dioxide-water solution was then prepared and slugs of the solution were injected, separated by injections of distilled water. When flowing the low concentrations of sulfur dioxide, two pore volume slugs were used. For concentrations over two per cent sulfur dioxide, only one pore volume size slugs were used.

A Ruska Model 2243-B111-UQ positive displacement constant rate proportioning pump was used to inject mercury into the mixing cylinder forcing the solution of sulfur dioxide and water into the core. The discharge rates of this pump could be varied by gear selection from 10 to 1200 cc per hour and was calibrated to 0.01 cc. The pump was manifolded such that the sulfur dioxide-water solution, oil or pure water could be pumped into the core. All lines in the system were 1/8 inch stainless steel with Autoclave fittings and needle valves. A schematic sketch of the apparatus used for the oil recovery and permeability tests is shown on Figure 3. The flow rate was constant throughout the injections and was as close to one pore volume per minute as the gear selection of the constant

FIGURE 3

SCHEMATIC SKETCH OF
FLOW APPARATUS

HEISE PRESS. GAUGE



BLEED-OFF
LINE

VACUUM PUMP

MERCURY
MANOMETER

BACK PRESS.
REGULATOR

REGULATOR

GAS BURETTES

SEPARATOR

LIMESTONE CORE
CONSTANT TEMP. CABINET

REGULATED
NITROGEN
SUPPLY

REGULATED
AIR SUPPLY

PROPANE
SUPPLY

REGULATED
CO₂

CALIBRATED
WATER TUBE

PENTANE

WATER
OR
SO₂
SOL'N

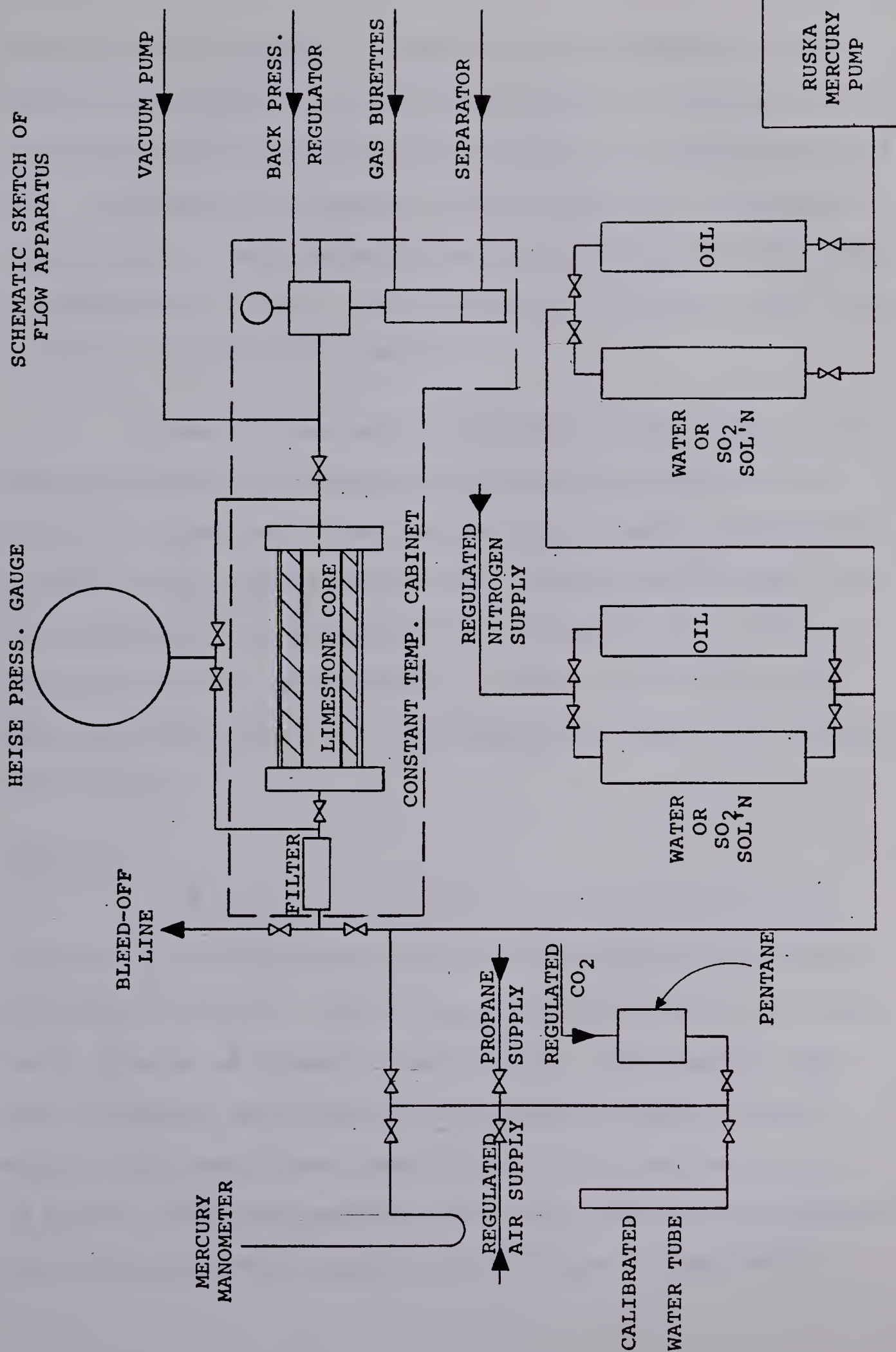
OIL

WATER
OR
SO₂
SOL'N

OIL

RUSKA
MERCURY
PUMP

HIGH PRESSURE TANKS



rate pump would permit. A 500 psi Heise pressure gauge was used to observe the upstream pressure. By the selection of valves the downstream pressure could be checked during a test. A Grove back pressure valve loaded with nitrogen was used to hold a back pressure on the effluent for the change in permeability tests. The pressure differential and volume of fluid injected were recorded.

Observations were also made on the effect of continually flowing solutions of low sulfur dioxide concentrations. Upwards of one hundred pore volumes were passed through a core during some tests. This type of a test was not conducted at a constant rate but rather at a near constant pressure differential. Tests of this type were continued until the flow rate became too rapid for accurate measurement.

Recovery

The alundum cores which were used for the oil recovery tests were cleaned by flushing them with pentane and methyl alcohol. Pentane was flushed through the cores until no sign of staining was evident. The pentane was then displaced using ten pore volumes of methyl alcohol and the core was blown down with air for a minimum of 12 hours. Repeated weighing and continued drying indicated that the cores would dry within 12 hours. Core Number

RA-7918 was evacuated and then saturated with distilled water. The void volume of the core was obtained by measuring the volume of water absorbed and was checked by weighing the core before and after saturating. The bulk volume of the core was obtained by measuring its dimensions.

The permeability of the core was obtained by injecting distilled water using the Ruska constant rate pump. When the permeability to water had been determined, the oil saturation was then established by injecting oil until water production ceased. By maintaining a constant material balance on the fluid injected and the fluid recovered, the oil and water saturations within the core could always be determined. When the only water within the core was immobile at the test conditions, which would occur by the time four pore volumes of oil had been introduced, the equipment was then made ready for simulated water flooding. Diesel fuel, Swan Hills crude oil and Turner Valley crude oil were used in separate tests as the hydrocarbon phase.

A back pressure of 70 psig was maintained by pressurizing a gas-liquid separator that was used to collect the effluent. Seventy psig is greater than the vapor pressure of any of the solutions used so that the displacing fluid was always in the liquid phase. It was

observed that the crude oil and the flood solution collected in the test tubes did not break clean. A slight emulsion formed making it impossible to observe the respective volumes of the two liquids. Two drops of Tretolite F-95 were added to each receiving tube and the liquids separated thereafter.

Upon the completion of a flood the core was resaturated with oil. Occasionally increased pump rates were required to reduce the water saturation to the desired level. When a series of tests were completed the core was flushed with five pore volumes of pentane followed by ten pore volumes of methyl alcohol. The core was dried by flowing air through it for 12 hours.

Alundum Core Number TA-7919 was treated with linoleic acid, a long chain fatty acid, to make it "oil wet". The degree of wettability was not determined. This core was prepared in the same manner as Core Number RA-7918 except the porosity was determined using methyl alcohol. After the porosity was calculated, a two per cent solution of linoleic acid and alcohol was injected and allowed to stand for 24 hours in the core. Following this, the core was handled in the same manner as Core Number RA-7918. Turner Valley and Swan Hills crude oil were used as the hydrocarbon in the tests.

Reaction Rate

To obtain some indication of the rate of reaction between the sulfur dioxide-water solution and limestone, numerous tests were conducted using core chips. A modified Baroid high pressure fluid loss cell, encased in an electrically heated temperature bath was used. A sample of limestone core from the Turner Valley oil field was crushed and the chips were sized by passing the chips through the 1/2 inch sieve and using those that were retained on the 3/8 inch sieve. Two hundred grams of the graded core chips were placed in the cell, the cell was filled with kerosene and then the cell and contents were brought up to the test temperature and pressure. Any pressure build up within the cell due to fluid expansion was observed. Sulfur dioxide-water solution was then introduced into the cell thereby displacing the oil. An aliquot was drawn off at two minute intervals during the first ten minutes, then at five minute intervals. After the aliquot was obtained it was quickly cooled to room temperature. The pH of the sample was then determined using a Beckman pH meter and the results plotted. This procedure was continued until the pH appeared constant. Tests were conducted at various temperatures and pressures using several concentrations of sulfur dioxide. The pH of each sulfur dioxide-water solution used was also obtained with the meter.

DISCUSSION OF RESULTS

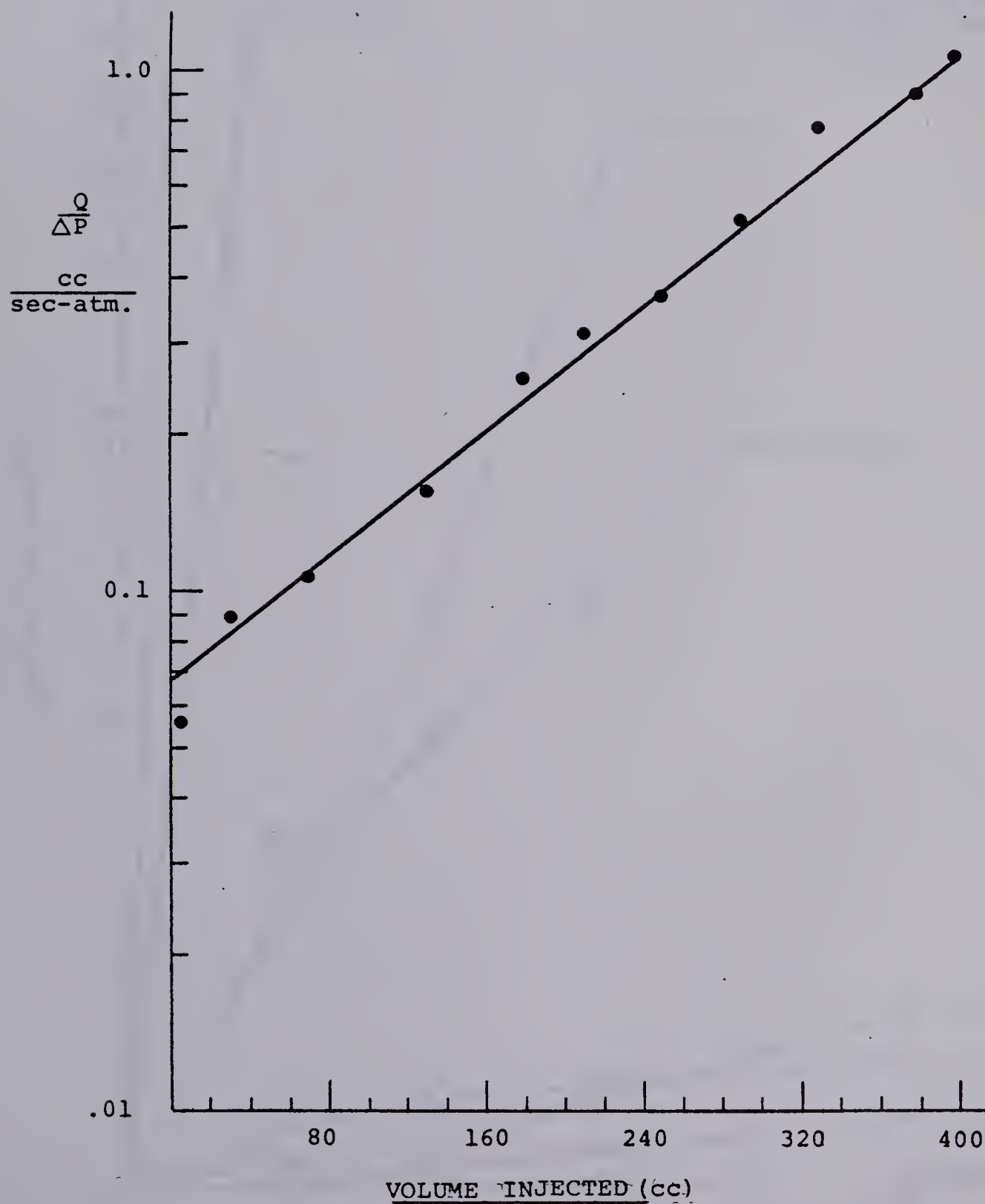
Change in Permeability

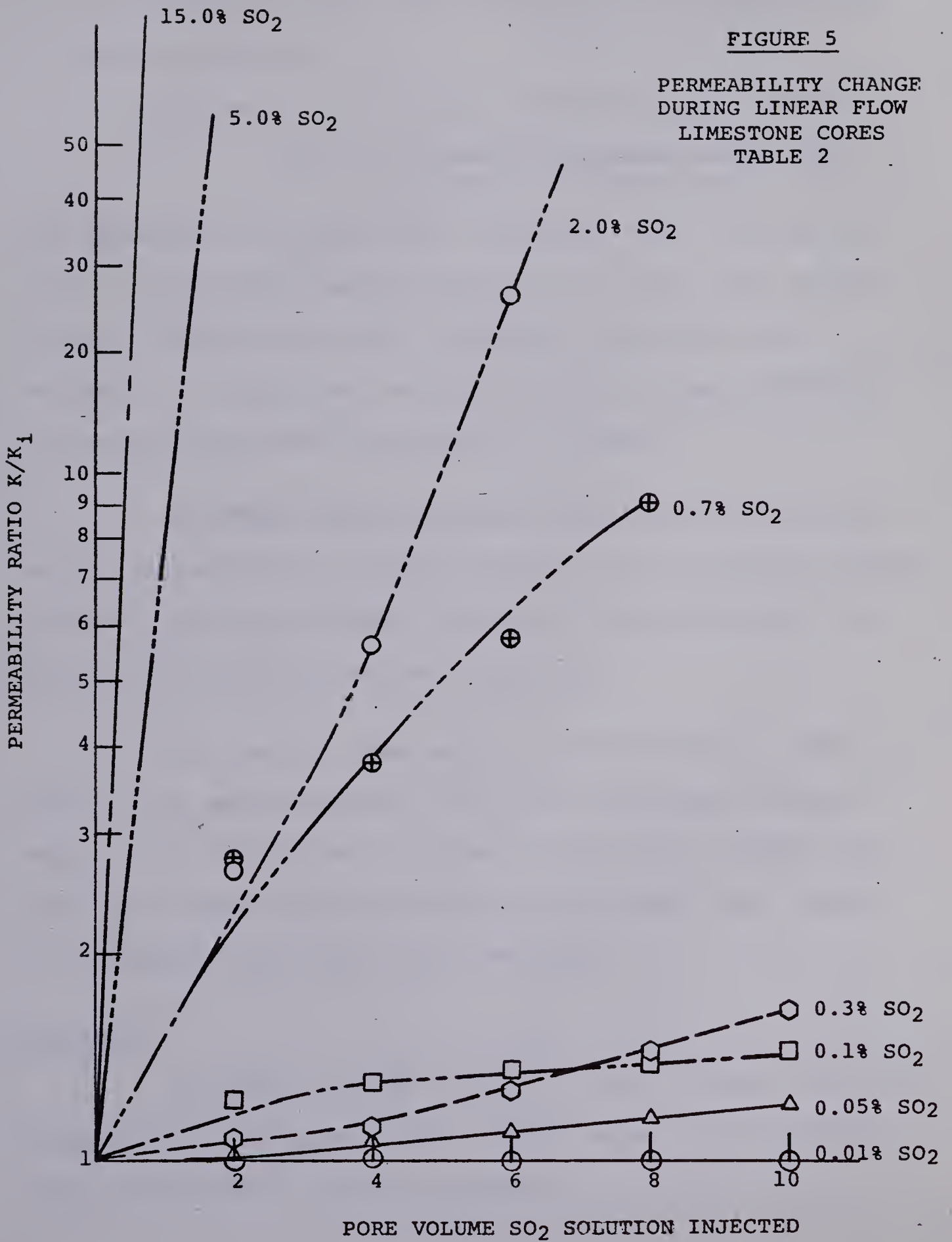
Work on this project began using the short linear limestone cores.* The effect of flowing various concentrations of the sulfur dioxide solution was obtained as well as the effect of flowing a large volume of a low concentration. The results are plotted on Figures 4 and 5. It was found that the permeability of a particular core would continue to increase as long as the solution was flowing through it. In general, the stronger solutions produced greater permeability increases for a given quantity of solution. This is illustrated in Figure 5. It appeared that up to 0.3 per cent sulfur dioxide, the reaction between the solution and the core was suppressed. Solutions containing over 0.3 per cent sulfur dioxide however had quite an influence on the core. Solutions over five per cent sulfur dioxide were strongly reactive with the core and usually by the time one pore volume of solution had been injected, the permeability had increased over one hundred times. Examination of the core after testing disclosed a channel had been etched through the length of the core by the stronger solutions.

* Refer to page A-32 for Core Description.

FIGURE 4

PERMEABILITY CHANGE
DURING LINEAR FLOW
- 0.2% BY VOL SO₂
- TEST NO. 4
- LIMESTONE CORE NO. 4-L





Flow studies using the radial flow cell gave a scattering of points when the data was plotted. Figure 6 is an example of data when plotting $Q/\Delta P$ versus volume of solution injected.

Where: Q = cubic centimeters per second

ΔP = injection pressure minus back pressure in atmospheres

The permeability of the core increased from 0.454 md to 0.581 md after 18.9 pore volumes of 0.04 per cent sulfur dioxide solution had been injected. After 18.9 pore volumes of 0.2 per cent sulfur dioxide had been injected the permeability had increased to 11.9 md.

Although the data from these radial flow tests were not consistent, it was evident that by flowing sulfur dioxide solutions through the radial limestone core the permeability of the core was improved.

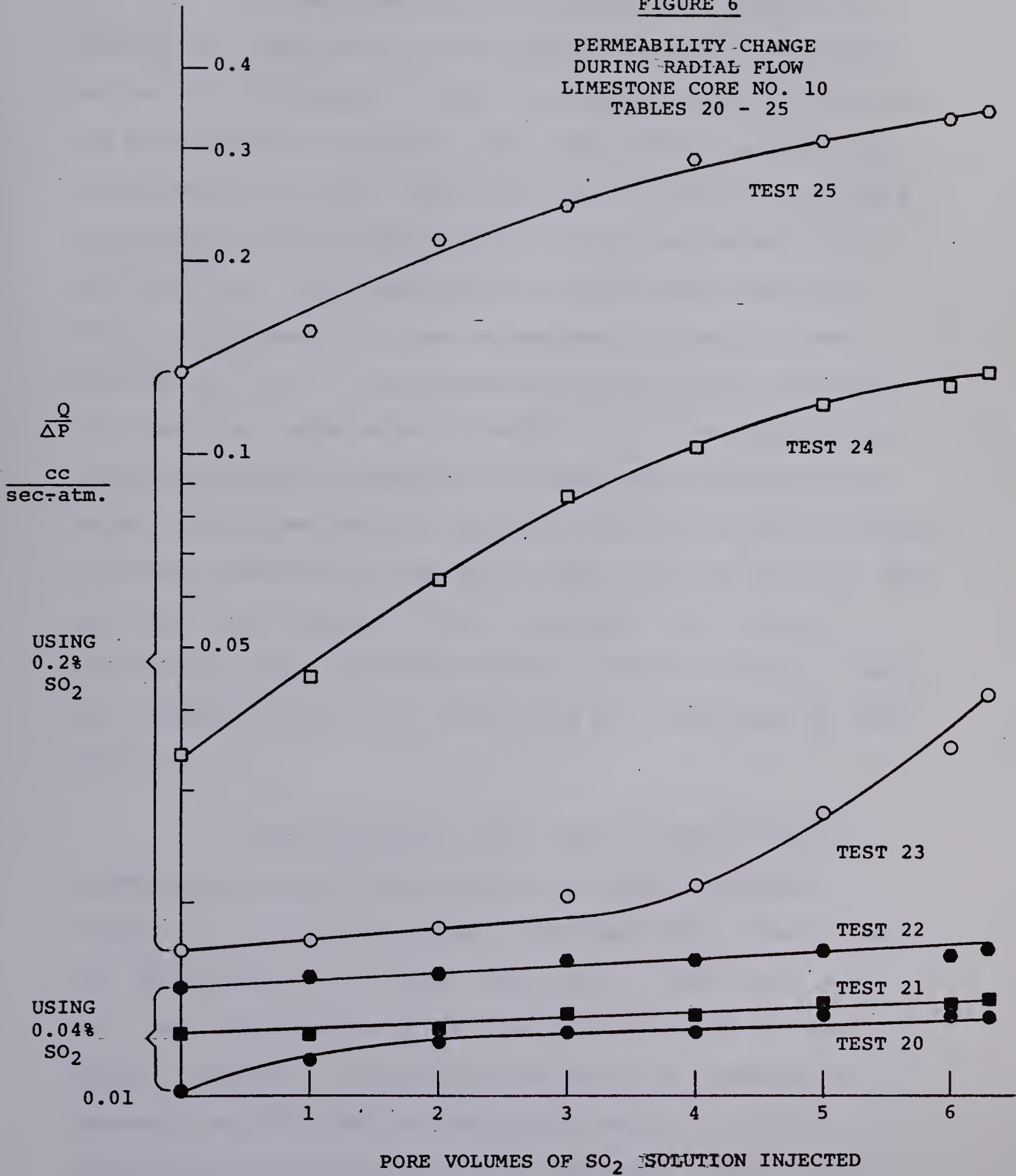
The radial flow cell was constructed in such a manner that approximately 177 cc of void space existed when the test core was in place. Since this volume was over four times the pore volume of the test core, radial oil recovery tests were not considered.

Recovery

By using alundum cores for the recovery tests the permeability and pore volume of the cores did not change appreciably during the test period.

FIGURE 6

PERMEABILITY CHANGE
DURING RADIAL FLOW
LIMESTONE CORE NO. 10
TABLES 20 - 25

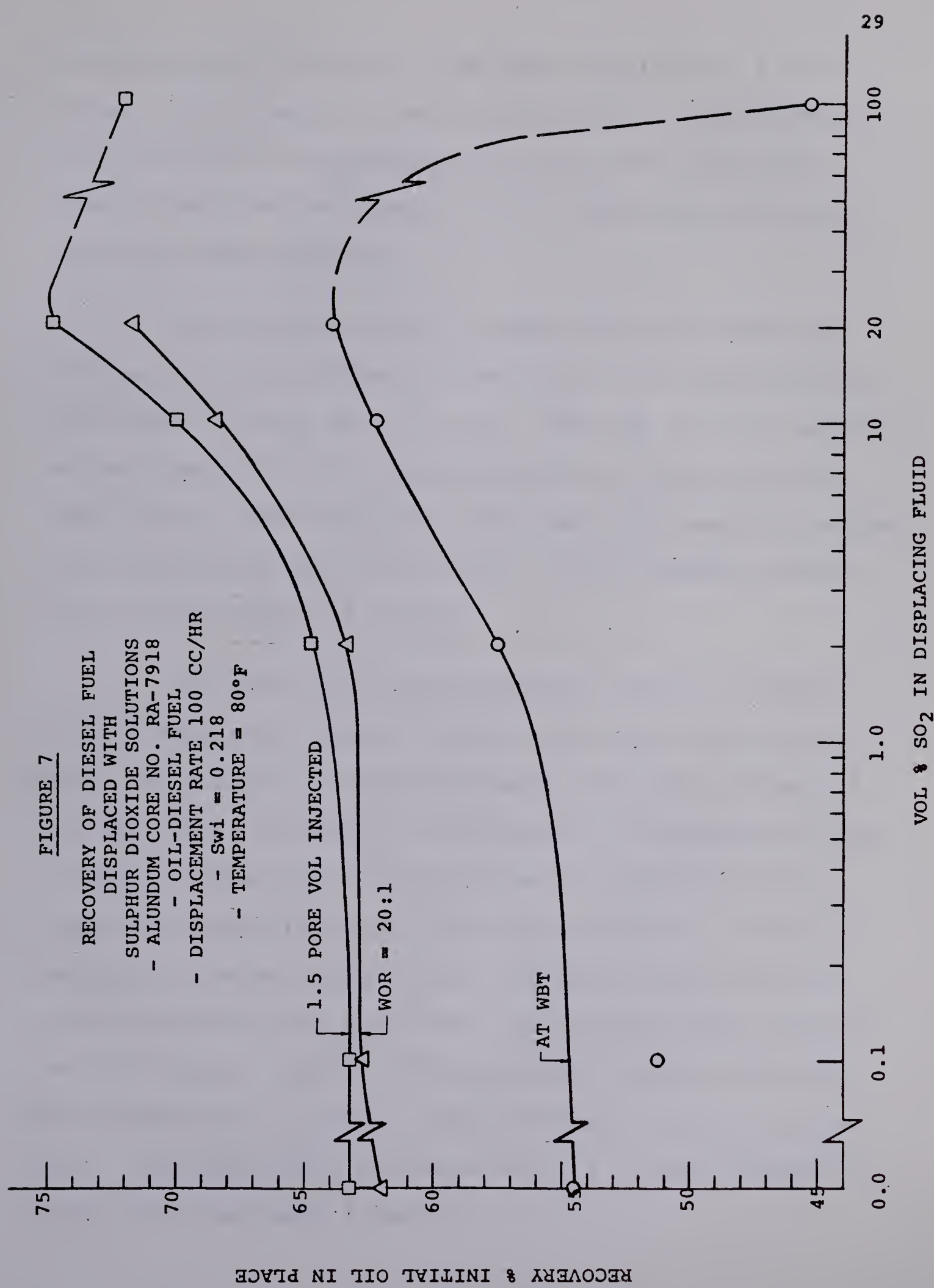


For the first series of flood tests conducted, diesel fuel was used as the hydrocarbon phase. The pore volume of Core Number RA-7918 was determined to be 60.0 cc by measuring the volume of water required to saturate the dried evacuated core. The dimensions of the core had been previously measured and the bulk volume was calculated to be 230.59 cc. After saturating the core with distilled water the permeability was determined by pumping water through the core. The permeability to water by averaging two tests was calculated to be 328.5 md. Ten tests were conducted using pressurized nitrogen gas to displace the water. Although pressure regulators were used and a constant pressure differential was maintained, the flow rate for each test was not constant. Since flow rate might have an influence on the percentage of oil recovered during a test, the results of these ten tests were not considered in this report.

A Ruska constant rate pump was used for the remaining tests and the injection rate held constant. Figure 7 is a plot of the data obtained using diesel fuel and displacing it with zero per cent, 0.1 per cent, 2.0 per cent, 10.0 per cent, 20.0 per cent and 100 per cent sulfur dioxide. According to the data, an increase in recovery was obtained as the concentration of sulfur dioxide in a water solution was increased. Pure sulfur

FIGURE 7

RECOVERY OF DIESEL FUEL
DISPLACED WITH
SULPHUR DIOXIDE SOLUTIONS
- ALUNDUM CORE NO. RA-7918
- OIL-DIESEL FUEL
- DISPLACEMENT RATE 100 CC/HR
- $S_{wi} = 0.218$
- TEMPERATURE = 80°F



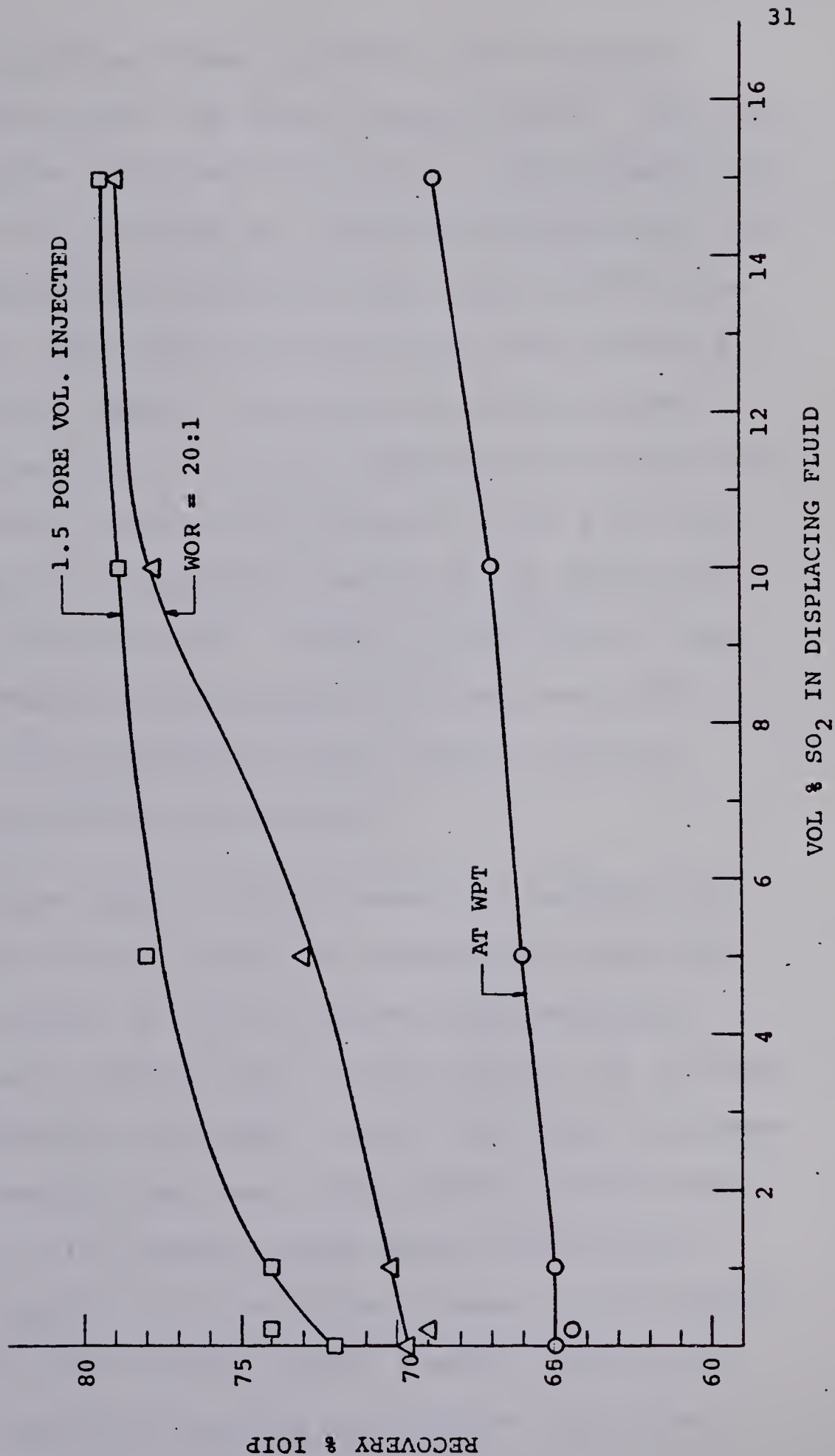
dioxide however is shown to be less efficient as a displacing fluid than a 20 per cent solution. The recovery at a WOR of 20:1 increased from 62 per cent when using zero per cent sulfur dioxide to 71.7 per cent when using the 20 per cent solution.

At the conclusion of these tests the core was flushed with 50 cc of pentane and 700 cc of methyl alcohol and purged with air for 12 hours. The dry core was weighed and was found to be 1.9 grams less than it was prior to these tests. This indicates there was some reaction between the alundum core and the solution. This reaction was not investigated during this work.

The core was resaturated with water in preparation for the next series of tests using Swan Hills crude oil. The results of the tests using Swan Hills crude oil are plotted in Figure 8. The increase in recovery at breakthrough, as the concentration of sulfur dioxide in the flood water was increased, was almost linear. The oil recovery increased from 65 per cent using zero per cent sulfur dioxide to 68.8 per cent oil recovery when using 15 per cent sulfur dioxide. The recovery obtained when the WOR reached 20:1 increased from 69.75 per cent to 79.0 per cent. The tests were terminated after 1.5 pore volumes of flood fluid had been injected.

FIGURE 8

- OIL SWAN HILLS CRUDE
- ALUNDUM CORE NO. RA-7918
- DISPLACEMENT RATE 100 CC/HR
- $S_{wi} = 0.333$
- TEMPERATURE = 150°F



Alundum Core Number TA-7919, which was made "oil wet", was used for the final recovery tests. The pore volume of the core was found to be 56 cc. The permeability to water prior to injecting any crude oil was 250 md. Swan Hills and Turner Valley crude oils were each used in Core Number TA-7919. The results of the tests were plotted on Figures 9 and 10. Figure 9 is a plot of data obtained using Swan Hills crude oil and by averaging the results of two water floods, averaging the results of two 1 per cent sulfur dioxide floods, and the results of one flood using ten per cent sulfur dioxide. Figure 10 is a plot of data obtained using Turner Valley crude oil displaced with; one per cent and ten per cent sulfur dioxide and the averaged results of two water floods.

Although only a limited amount of testing was done using the "oil wet" core, it was apparent that the results were similar to those obtained when using the "water wet" core. The per cent of the initial oil in place which was recovered, increased 9.5 per cent with the Turner Valley crude and by 6 per cent with the Swan Hills crude. The increase in oil recovery noted during these tests could be the result of the reaction of some of the components of the oil with sulfur dioxide thereby reducing the interfacial tension between the oil and the displacing

FIGURE 9

RECOVERY OF SWANHILLS CRUDE
FROM "OIL WET" CORE
- ALUNDUM CORE NO. TA-7919
- DISPLACEMENT RATE 100 CC/HR
- $S_{wi} = 0.256$
- TEMPERATURE = 150°F

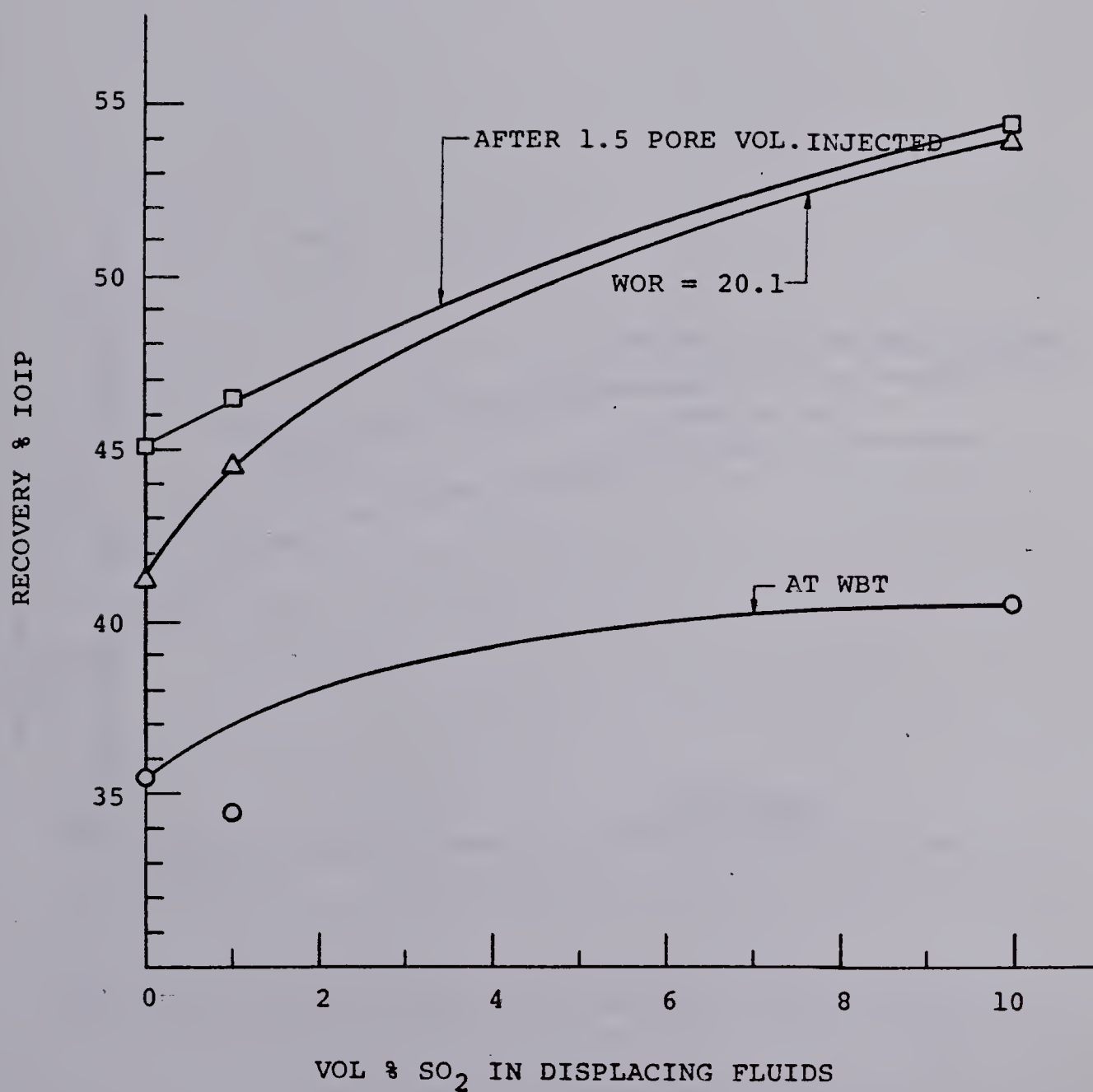
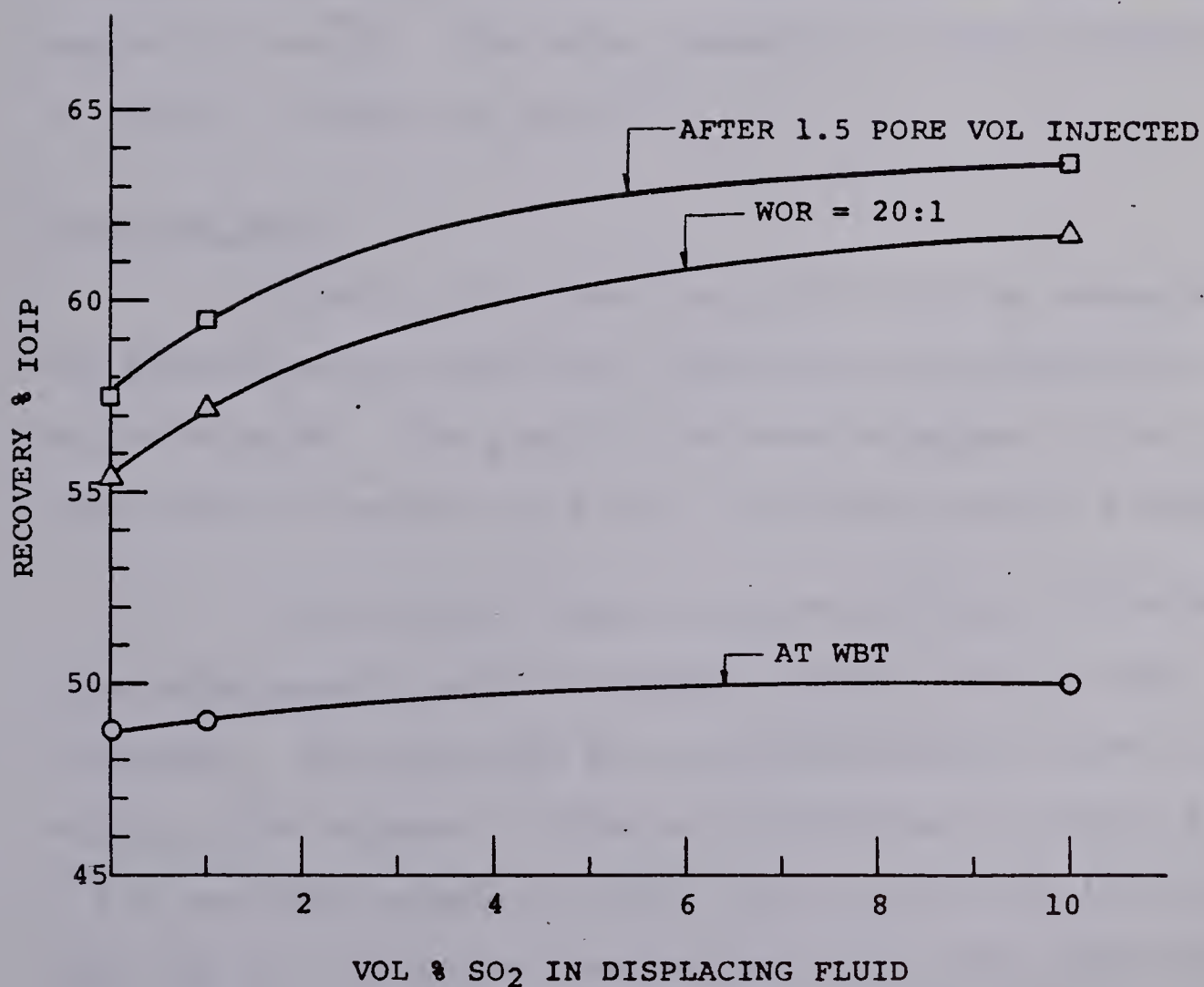


FIGURE 10

RECOVERY OF TURNER VALLEY CRUDE
FROM "OIL WET" CORE
- ALUNDUM CORE NO. TA-7919
- DISPLACEMENT RATE 100 CC/HR.
- $S_{wi} = 0.304$
- TEMPERATURE = 150 °F



fluid. It is also possible that sulfur dioxide would reduce the viscosity of both the oil and the displacing fluid.

Laboratory floods using carbon dioxide produced additional oil when the pressure of the model reservoir was reduced to atmospheric. This was termed blow-down recovery⁽¹¹⁾. No blow-down recovery was noted during any of the recovery tests using sulfur dioxide. This is probably due to the low vapor pressure of sulfur dioxide. Carbon dioxide at its critical temperature, 88°F, has a vapor pressure of 1070 psia. This provides an appreciable amount of energy. The vapor pressure of sulfur dioxide at 150°F, is only 181 psia⁽¹⁰⁾.

Reaction Rate

Figure 11 is a semi log plot of pH as measured on the Bechman meter versus the logarithmic concentration of sulfur dioxide. The plot of the results appear to be a straight line over the range of 0.1 to 1.0 per cent sulfur dioxide.

The reaction tests using core chips indicated that solutions of sulfur dioxide reacted readily with limestone. The solution at all concentrations spent itself within a few minutes. This is illustrated on Figure 12. A 0.2 per cent solution, which had a pH of 1.85 initially, had a pH of 4.06 after reacting with the core chips for

FIGURE 11

pH OF UNREACTED SOLUTION
VERSUS
CONCENTRATION IN
WEIGHT PERCENT
TEMPERATURE 21°C

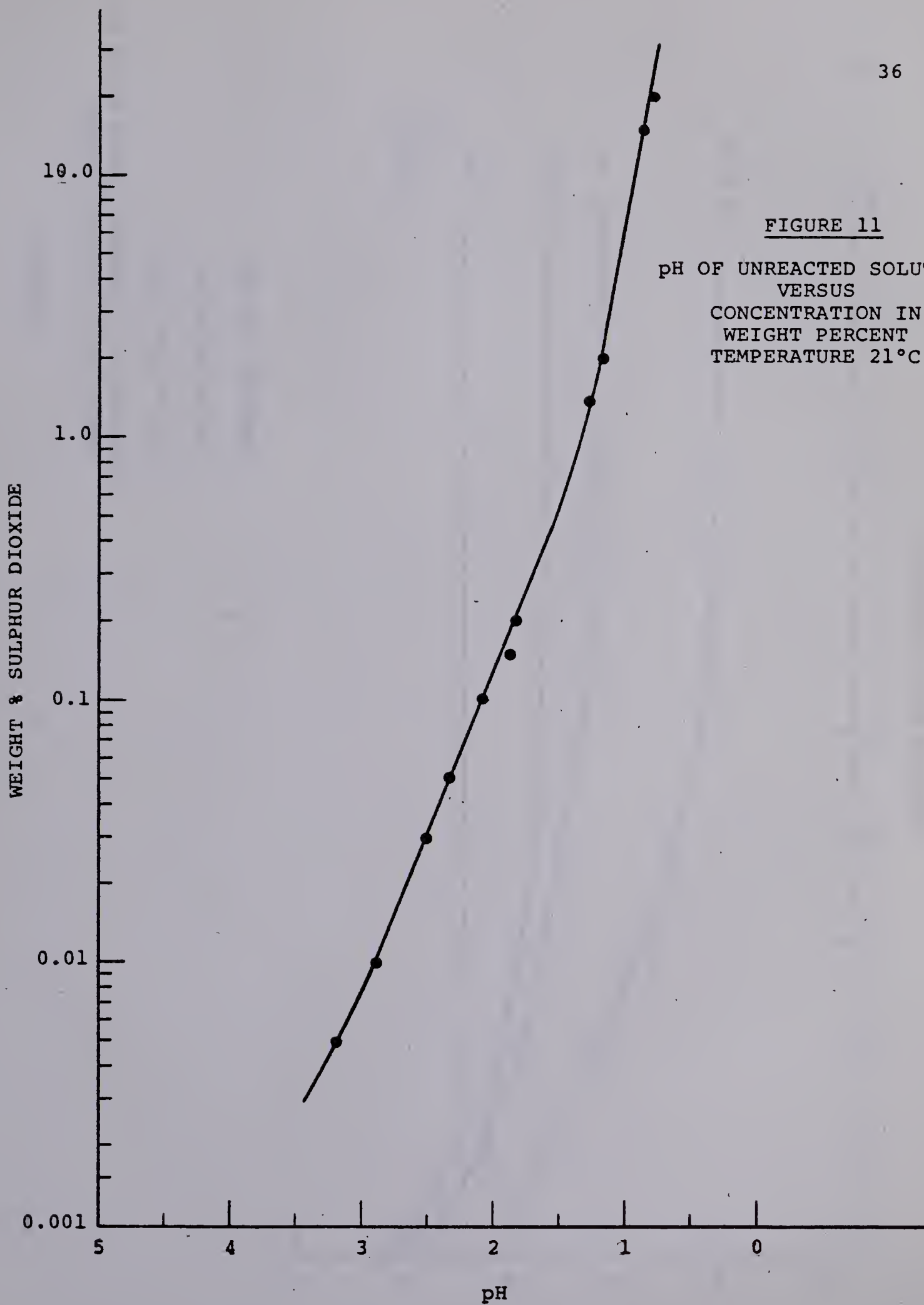


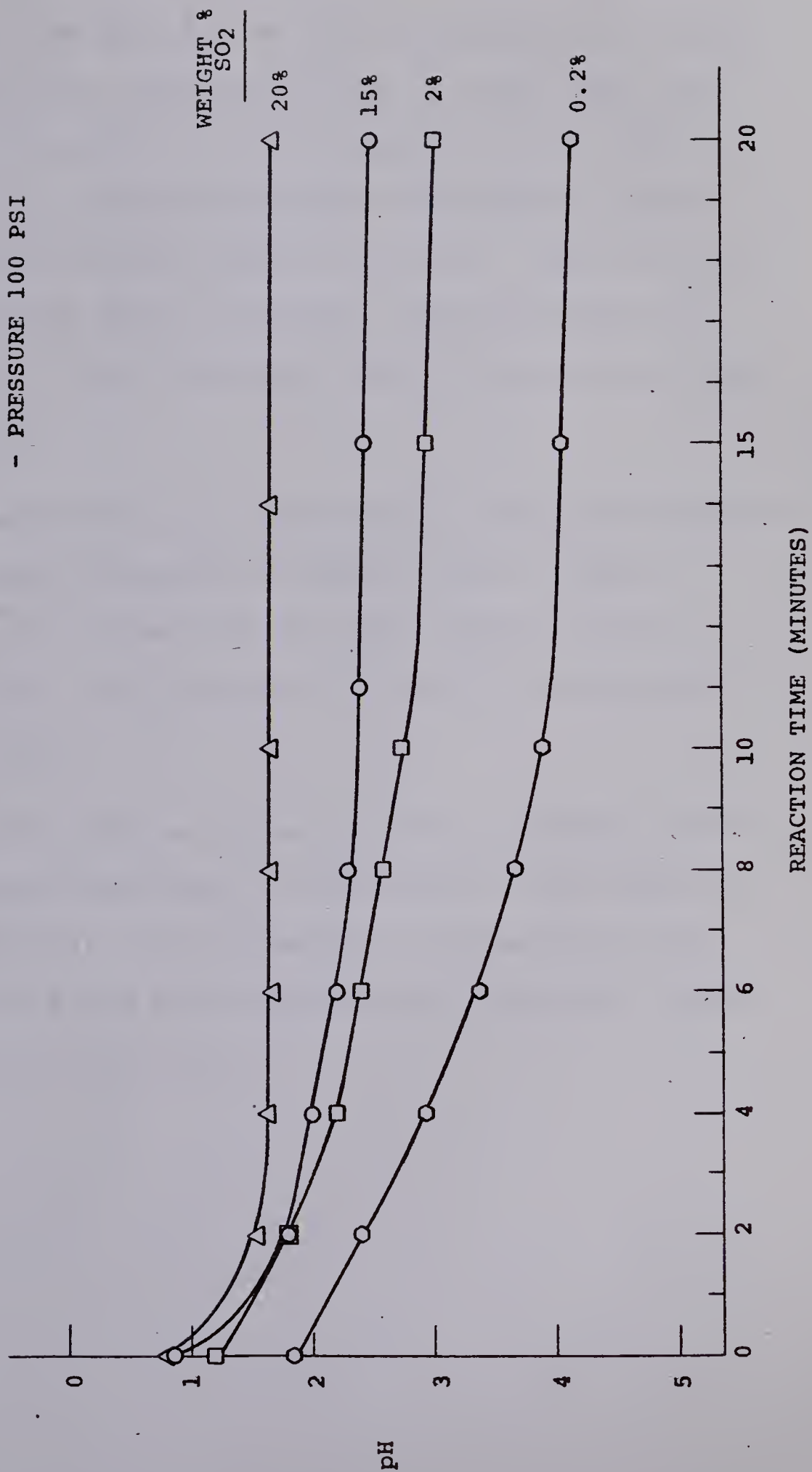
FIGURE 12

REACTION OF SULPHUR DIOXIDE
SOLUTIONS ON LIMESTONE CHIPS AT 75 °F

- 200 gm CORE CHIPS

- 110 cc SOLUTION

- PRESSURE 100 PSI



20 minutes. A 20 per cent solution, also shown in Figure 12, increased in pH from 0.8 to 1.65 within the first four minutes. During the remainder of the 30 minute test, the pH gradually increased to a final value of 1.75. This indicated change in rate of reaction was probably due to a buffering action of the reaction products. Each of the four concentrations tested responded similarly with the change in reaction rate occurring later in the test for the weaker solutions.

By increasing the temperature of the reaction cell there was a slight increase in reaction rate. This is shown on Figure 13. The 72°F and 200°F tests were conducted at 50 psig. The pressure remained at 200 psig during the 250°F test.

Data obtained at three different pressures indicated that pressure had very little effect on the rate of reaction (Figure 14). The temperature was held at 75°F and the reaction tests were conducted at atmospheric pressure, 340 psig and 1200 psig.

FIGURE 13

REACTION OF SULPHUR DIOXIDE
ON LIMESTONE CHIPS AT
VARIOUS TEMPERATURES

- 200 gm CORE CHIPS

- 110 cc SOLUTION

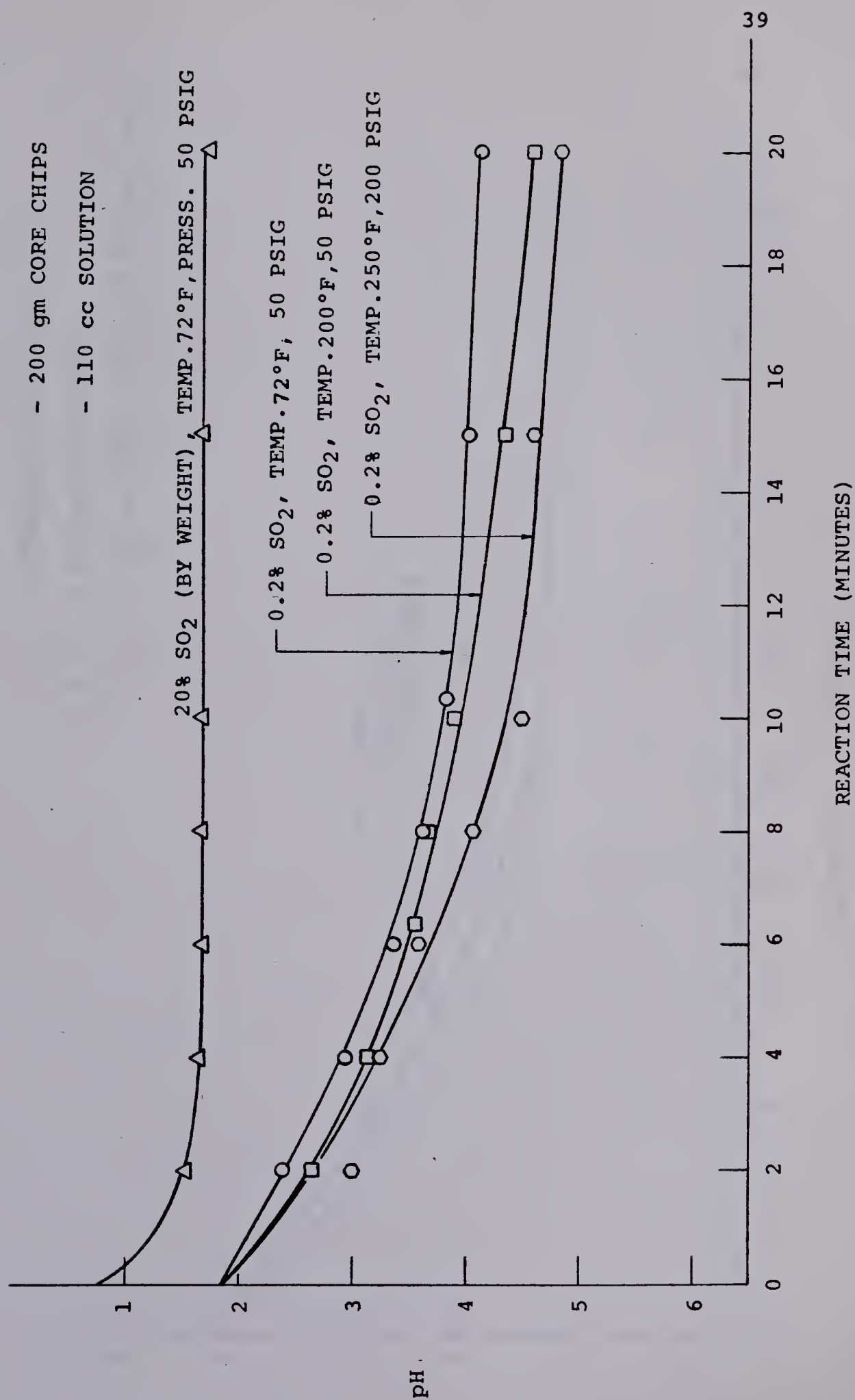
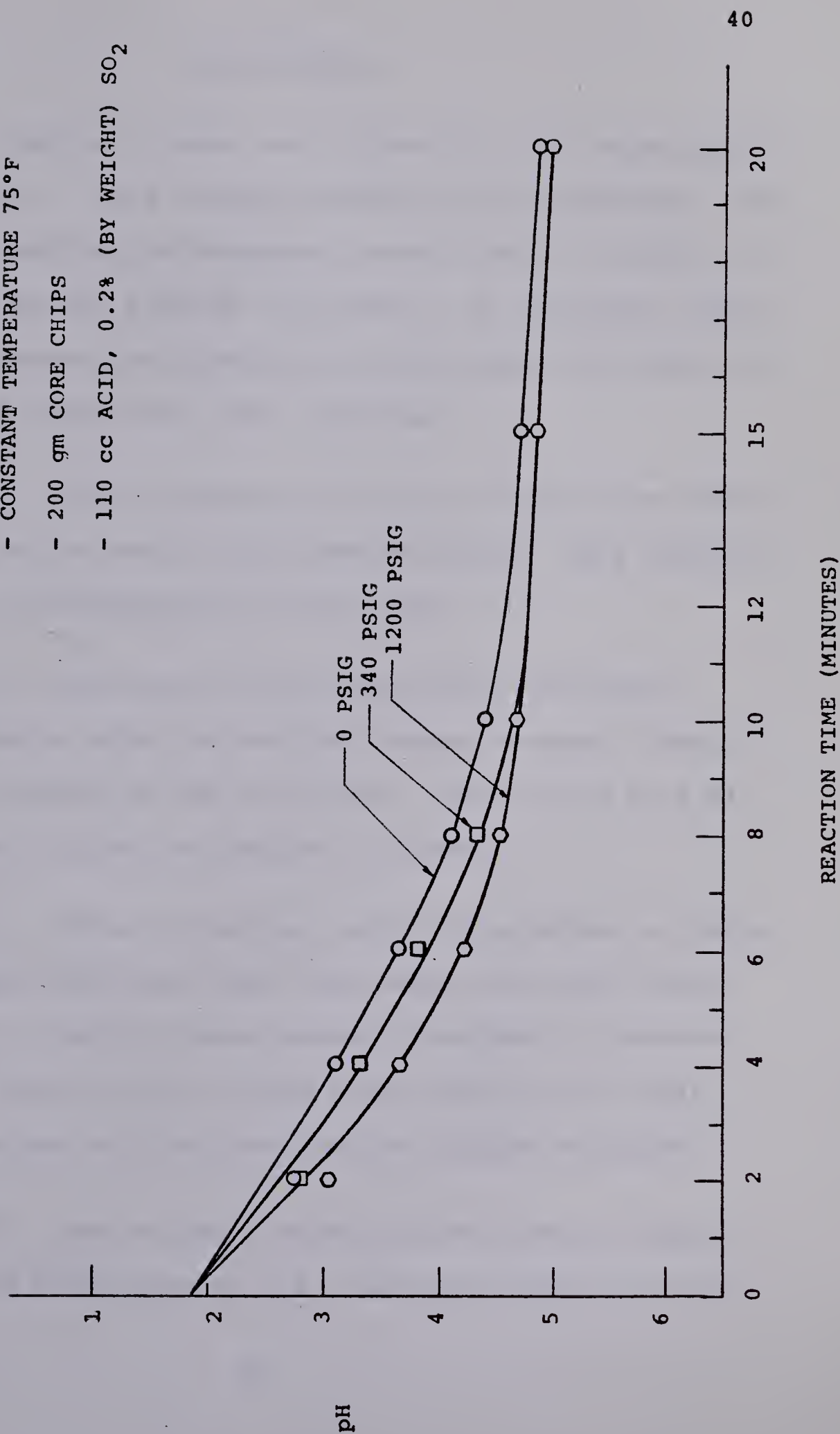


FIGURE 14

REACTION OF SULPHUR DIOXIDE SOLUTIONS
ON LIMESTONE CHIPS AT VARIOUS
PRESSURES

- CONSTANT TEMPERATURE 75°F
- 200 gm CORE CHIPS
- 110 cc ACID, 0.2% (BY WEIGHT) SO_2



CONCLUSIONS

Reservoir rocks are in general very heterogeneous and therefore, rigid conclusions may not be justified. The following qualitative statements were made with regard to the use of sulfur dioxide solutions as an injection fluid. These statements are restricted to the materials used and the limited laboratory tests performed.

1) Water solutions of sulfur dioxide are acidic in nature and do react with limestone rock. This reaction increases the permeability of the rock.

2) Solutions of over five per cent sulfur dioxide reacted with the rock to produce channels through the entire length of the test core. These cores were all approximately eight centimeters in length.

3) Water containing sulfur dioxide has a higher displacement efficiency than pure water for water flood operations. Specific tests showed increases in recovery from 69.75 per cent for a pure water flood to 79.0 per cent when using a 15 per cent sulfur dioxide solution.

4) Pure sulfur dioxide did not have as great a displacement efficiency as did a saturated water solution.

5) Blow-down recovery from sulfur dioxide would be limited compared to the amount reported to be produced when using carbon dioxide.

6) An increase in temperature accelerates the reaction between the solution and limestone.

7) The rate of reaction between the solution and limestone reduces as the reaction proceeds.

RECOMMENDATIONS

There must be a continuing search for methods and materials that will increase the amount of recoverable oil from any given reservoir. The work performed in this project has been an attempt to determine the effect of using sulfur dioxide. Although the results of this work indicate a slight increase in recovery, further investigations are warranted.

To reduce the number of variables when working with this acidic solution, future recovery tests should be conducted using an artificial reservoir, possibly composed of silica sand or glass beads.

Since the solution reacts with limestone, field tests of this material to determine recovery might be restricted to sandstone formations that are not cemented with calcareous material.

Additional tests should be carried out to determine the results of exposing the solution to limestone over an extended period of time. Would the reaction products buffer the solution sufficiently to virtually halt the reaction after some period of time?

NOMENCLATURE

A	- Cross-sectional area in square centimeters.
API	- American Petroleum Institute.
atm	- Atmospheres.
BBL	- Barrel.
C	- Centigrade degrees temperature.
cc	- cubic centimeter.
cm	- Centimeter.
F	- Fahrenheit degrees temperature.
GOR	- Gas oil ratio.
hr.	- Hour.
Hg	- Mercury.
IOIP	- Initial oil in place
K	- Permeability in millidarcies.
K_i	- Initial permeability in millidarcies.
L	- Length in centimeters.
md	- Millidarcies.
ml	- Millilitre.
mins.	- Minutes.
pH	- Logarithm of the reciprocal of the hydrogen ion concentration.
psi	- Pounds per square inch.
psia	- Pounds per square inch absolute.
psig	- Pounds per square inch gauge.

PV	- Pore volume.
ΔP	- Pressure differential in atmospheres or pounds per square inch.
Q	- Flow rate in cubic centimeters per second.
sec.	- Seconds.
SCF	- Standard cubic feet (14.7 psia, 60°F).
S_{wi}	- Interstitial water saturation as a fraction of pore volume.
t	- Temperature.
ΔT	- Time interval in seconds.
Vol.	- Volume.
WBT	- Water Breakthrough
WOR	- Water Oil Ratio
%	- Per cent
ϕ	- Porosity Fraction
°	- Degree

BIBLIOGRAPHY

1. Campbell, W.B. and Maass, O.: "Equilibria in Sulfur Dioxide Solutions", Canadian Journal of Research, (1930), Vol. 2, p42.
2. Falk, M. and Giguere, P.A.: "On the Nature of Sulfurous Acid", Canadian Journal of Chemistry, (1958), Vol. 36, p1121-1125.
3. Morgan, O.M. and Maass, O.: "An Investigation of the Equilibria Existing in Gas-Water Systems Forming Electrolytes", Canadian Journal of Research, (1931), Vol. 5, p162-181-196.
4. Davis, D.S.: "Nomogram: Viscosity of Liquid Sulfur Dioxide", Chemical and Process Engineering, (October, 1958), Vol. 39, No. 10.
5. Fazil, M.: "High Viscosity Crude Oil Displacement in a Long Unconsolidated Natural Sand Pack Using Carbonated Brine", M.Sc. Thesis, Unpublished, University of Alberta, (1965).
6. Flock, D.L. and Scott, J.: "The Effects of Sulfur Dioxide Solvent Flooding on Limestone Cores", Unpublished, University of Alberta, (1960).
7. Gatlin, C.: "Petroleum Engineering: Drilling and Well Completions", Chapter 10, Prentice Hall Inc., (1960).
8. Hengstebeck, R.J.: "Petroleum Processing, Principles and Applications", New York, McGraw-Hill Book Company, Inc., (1959), Chapter 4, p71-72.
9. "International Critical Tables", McGraw-Hill Book Company Inc., (1928), Vol. 111.
10. Lange, N.A.: "Handbook of Chemistry", Fifth Edition, Handbook Publishers Inc., (1944), p1258 and 1437.
11. Martin, J.W.: "Additional Oil Production Through Flooding with Carbonated Water", Producers Monthly, (July, 1951), Vol. 15, No. 9, p18-22.
12. Martin, J.W.: "The Use of Carbon Dioxide for Increasing the Recovery of Oil", Quarterly Bulletin, The Interstate Oil Compact Commission, (April, 1951), Vol. X, No. 1, p50-54.

13. Muskat, M.: "What is the Future of Production Technology for Research", Journal of Petroleum Technology, (April, 1956).
14. Natural Gas Supply Men's Association, "Data Book".
15. Perry, John H.: "Chemical Engineers Handbook", Third Ed., McGraw-Hill Book Company Inc., (1950).
16. Plummer, A.W.: "Thermodynamic Data for System $\text{SO}_2\text{-H}_2\text{O}$ ", Chemical Engineering Progress, (1950), Vol. 46, No. 7, p369-374.
17. Pirson, S.J.: "Oil Reservoir Engineering", Chapter 2, McGraw-Hill Book Company Inc., (1958).
18. Sisler, H.H.; Vanderwerf, C.A. and Davidson, A.W.: "General Chemistry: A Systematic Approach", The MacMillan Co., New York, (1949), p469.
19. Spall, B.C.: "Phase Equilibriums in the System Sulfur Dioxide-Water from 25-300°C.", Canadian Journal of Chemical Engineering, 41, p79-83 (1963).
20. Torrey, P.D.: "History and Significance of Fluid Injection in the United States", Improving Oil Recovery, University of Texas, (1957).
21. Torrey, P.D.: "New Techniques for Improving Oil Recovery", Improving Oil Recovery, University of Texas, (1957).
22. Wells, F.L. and MacClaren, R.H.: "Total Pressures for the System: Sulfur Dioxide-Water", TAPPI, (1955), Vol. 38, No. 11, p668-671.

APPENDIX

TABLE 1
 VALUES FOR CONSTANTS a AND b AS GIVEN
 BY WELLS AND MACCLAREN(22)

Constants in the equation $\text{Log } P_m = b \log P_w + a$

Where: P_m = total $\text{SO}_2\text{-H}_2\text{O}$ system pressure at $t^\circ\text{C}$, mm Hg
 P_w = vapor pressure of H_2O at $t^\circ\text{C}$, mm Hg
 a, b = constants

<u>Grams SO_2 per 100 ml Solution</u>	<u>a Intercept</u>	<u>b Slope</u>
0.3	0.0336	0.9865
0.05	0.0547	0.9805
0.08	0.842	0.9751
0.10	0.1094	0.9681
0.15	0.1744	0.9518
0.498	0.6160	0.8282
0.994	0.9240	0.7600
1.98	1.2952	0.6832
2.95	1.5135	0.6473
3.92	1.6448	0.6438
4.88	1.7546	0.6358
5.81	1.8537	0.6260
7.65	1.9865	0.6250
9.51	2.0944	0.6183
3.0	1.65	0.612
6.1	2.00	0.565
7.8	2.16	0.543

TABLE 1 (Continued)

VALUES FOR CONSTANTS a AND b AS GIVEN
BY WELLS AND MACCLAREN(22)

<u>Grams SO₂</u> <u>per 100 ml Solution</u>	<u>a</u> <u>Intercept</u>	<u>b</u> <u>Slope</u>
10.3	2.30	0.526
12.1	2.40	0.512
16.2	2.54	0.505
18.9	2.63	0.491
22.7	2.69	0.497
Two-phase (35 % over-all)	2.72	0.531
100	2.68	0.566

TABLE 2

SUMMARY OF LINEAR FLOW TESTS OBSERVING
CHANGE IN PERMEABILITY

<u>Test No.</u>	<u>Volume % of SO₂</u>	<u>Core No.</u>	<u>Pore Vol. (cc)</u>	<u>K_i (md)</u>	<u>Pore Vol. Injected</u>	<u>K (md)</u>	<u>K/K_i</u>
1	0.01	6	7.1	91.0	10	91.0	1.00
2	0.05	6	7.1	91.0	10	109.0	1.20
3	0.1	16	6.7	28.5	10	39.3	1.38
4	0.2	4-L	3.3	73.0	120	2,280	31.3
5	0.3	6	7.1	112.5	10	189.0	1.68
6	0.7	13	5.7	44.7	10	835	18.7
7	2.0	14	4.6	52.5	10	3,150	60.0
8	5.0	4	7.0	83.4	2	13,300	159.5
9	5.0	5	6.8	19.5	1	2,530	130.0
10	15.0	7	6.3	19.3	1	2,500	129.5

TABLE 3

SUMMARY OF RADIAL FLOW TESTS OBSERVING
CHANGE IN PERMEABILITY

Core No. 10

Outside Diameter = 11.049 cm

Pore Volume = 63.5 cc

Length = 9.576 cm

<u>Test No.</u>	<u>Volume % of SO₂</u>	<u>Initial Q/ΔP (cc/sec-atm)</u>	<u>Pore Vol. Injected</u>	<u>Final Q/ΔP (cc/sec-atm)</u>	<u>$\frac{Q/\Delta P}{(Q/\Delta P)_i}$</u>
20	.04	0.0102	6.3	0.0132	1.290
21	.04	0.0126	6.3	0.0141	1.120
22	.04	0.0148	6.3	0.0169	1.140
23	0.2	0.0169	6.3	0.0422	2.50
24	0.2	0.0338	6.3	0.1350	4.00
25	0.2	0.1340	6.3	0.345	2.57

TABLE 4SOLUBILITY OF SO₂ IN TURNER VALLEY CRUDE

<u>Pressure (psia)</u>	<u>Temperature (°F)</u>	<u>Vol. of SO₂ in Crude Sample (ml)</u>	<u>Vol. of Crude (ml)</u>	<u>Solubility (SCF/B)</u>
233	70.7	395.2	4.95	537
434	70.7	368.0	3.2	775
534	70.7	407.2	3.4	806
1,035	70.7	407.6	3.6	764
1,035	70.7	401.3	3.5	772
1,535	70.7	386.9	3.6	724
1,838	71.7	392.0	3.7	714

TABLE 5

SOLUBILITY OF SO₂ IN SWAN HILLS CRUDE

<u>Pressure</u> <u>(psia)</u>	<u>Temperature</u> <u>(°F)</u>	<u>Vol. of SO₂ in</u> <u>Crude Sample</u> <u>(ml)</u>	<u>Vol. of Crude</u> <u>(ml)</u>	<u>Solubility</u> <u>(SCF/B)</u>
133	70.6	399.8	2.85	946
234	70.6	417.9	2.95	955
534	70.6	413.6	2.95	946
1,034	70.6	405.0	2.85	937

TABLE 6

PRESSURE-VOLUME DATA FOR CORE NO. 4-L

Limestone

Pore Volume = 3.3 cc

Length = 7.83 cm

Cross Sectional Area = 5.06 cm²

Test No. 4

Temperature 76°F

Vol. Injected (cc)	P S I G			Time Sec.		Q/ Δ P (cc/sec-atm)
	<u>Inlet</u>	<u>Outlet</u>	<u>ΔP</u>	<u>Total</u>	<u>ΔT</u>	
water only						
5	88.5	78.75	9.75	135	135	.0559
0.2% SO ₂						
30	100.0	79.5	20.5	240	240	.0895
70	100.0	79.5	20.5	508	268	.1070
130	100.0	79.5	20.5	786	278	.155
180	100.0	80.0	20.0	931	145	.254
210	100.5	80.0	20.5	1,000	69	.312
250	100.5	80.0	20.0	1,080	80	.368
290	100.0	80.75	19.25	1,140	60	.510
330	100.0	82.5	17.5	1,188	44	.764
380	100.0	82.5	17.5	1,235	47	.894
400	100.0	82.5	17.5	1,251	16	1.050

TABLE 7

PRESSURE-VOLUME DATA FOR CORE NO. 6

Limestone

Length = 7.95 cm

Temperature 76°F

Area = 5.19 cm²

Porosity = 17.3%

Pore Volume = 7.1 cc

Injection Rate = 400 cc per hour

Test No. 1

<u>Pore Vol. Injected</u>		<u>P S I G</u>			<u>Permeability</u>	<u>K/K_i</u>
<u>Water</u>	<u>0.01% SO₂</u>	<u>Inlet</u>	<u>Outlet</u>	<u>Δ P</u>	<u>(md)</u>	
10		92.5	65.0	27.5	91.0	1.00
	2					
5		92.5	65.5	27.0	92.8	1.02
	2					
5		94.0	66.5	27.5	91.0	1.00
	2					
5		92.0	64.0	28.0	89.5	0.99
	2					
5		95.0	66.0	29.0	86.5	0.95
	2					
5		96.5	67.5	29.0	86.5	0.95
Flush with 100 pore volumes of water						
		92.3	64.8	27.5	91.0	1.00

TABLE 7 (Continued)
PRESSURE-VOLUME DATA FOR CORE NO. 6

Test No. 2

<u>Pore Vol. Injected</u>		<u>P S I G</u>			<u>Permeability</u>	<u>K/K_i</u>
<u>Water</u>	<u>0.05% SO₂</u>	<u>Inlet</u>	<u>Outlet</u>	<u>Δ P</u>	<u>(md)</u>	
10		92.5	65.0	27.5	91.0	1.00
	2					
5		92.8	65.5	27.3	91.9	1.01
	2					
5		92.5	67.0	25.5	98.1	1.08
	2					
5		92.5	67.5	25.0	100.0	1.10
	2					
5		92.5	68.8	23.7	105.3	1.16
	2					
5		89.8	66.8	23.0	109.0	1.20

Flush with 100 pore volumes of water

TABLE 7 (Continued)

PRESSURE-VOLUME DATA FOR CORE NO. 6Test No. 5

<u>Pore Vol. Injected</u> <u>Water</u>	<u>0.3 % SO₂</u>	<u>P S I G</u>			<u>Permeability</u> <u>(md)</u>	<u>K/K_i</u>
		<u>Inlet</u>	<u>Outlet</u>	<u>Δ P</u>		
5		95.0	72.8	22.2	112.5	1.00
	2					
5		93.5	72.8	20.7	120.5	1.07
	2					
5		92.0	72.8	19.2	130.0	1.16
	2					
5		90.5	73.0	17.5	143.0	1.27
	2					
5		88.5	73.0	15.5	161.5	1.44
	2					
5		86.8	73.5	13.3	189.0	1.68

TABLE 8

PRESSURE-VOLUME DATA FOR CORE NO. 13

Limestone

Length = 7.98 cm

Temperature 76°F

Area = 5.19 cm²

Porosity = 13.7%

Pore Volume = 5.7 cc

Injection Rate = 400 cc per hour

Test No. 6

<u>Pore Vol. Injected</u>		<u>P S I G</u>			<u>Permeability</u>	<u>K/K_i</u>
<u>Water</u>	<u>0.7% SO₂</u>	<u>Inlet</u>	<u>Outlet</u>	<u>Δ P</u>	<u>(md)</u>	
60		105.0	69.0	36.0	69.5	1.00
	2					
5		84.0	71.0	13.0	193.0	2.78
	2					
5		80.5	71.0	9.5	264.0	3.80
	2					
5		78.3	72.0	6.3	400.0	5.75
	2					
5		76.8	72.8	4.0	627.0	9.02
	2					
5		76.5	73.5	3.0	835.0	12.00

TABLE 9PRESSURE-VOLUME DATA FOR CORE NO. 14

Limestone Length = 7.93 cm
 Temperature 76°F Area = 5.19 cm²
 Porosity = 11.2% Pore Volume = 4.6 cc
 Injection Rate = 300 cc per hour

Test No. 7

<u>Pore Vol. Injected</u>		<u>P S I G</u>			<u>Permeability</u>	<u>K/K_i</u>
<u>Water</u>	<u>2% SO₂</u>	<u>Inlet</u>	<u>Outlet</u>	<u>ΔP</u>	<u>(md)</u>	
40		119.0	74.0	45.0	52.5	1.00
	2					
5		93.5	76.5	17.0	139.0	2.65
	2					
5		84.0	76.0	8.0	295.0	5.62
	2					
5		81.0	78.5	2.5	945.0	18.00
	2					
5		79.8	79.0	0.8	3150.0	60.00

TABLE 10PRESSURE-VOLUME DATA FOR CORE NO. 16

Limestone

Length = 8.0 cm

Temperature 75°F

Area = 5.19 cm²

Porosity = 13.7%

Pore Volume = 6.7 cc

Injection Rate = 400 cc per hour

Test No. 3

<u>Pore Vol. Injected</u> <u>Water</u>	<u>0.1% SO₂</u>	<u>P S I G</u>			<u>Permeability</u> <u>(md)</u>	<u>K/K_i</u>
		<u>Inlet</u>	<u>Outlet</u>	<u>ΔP</u>		
20		164.0	75.0	89.0	27.3	1.00
	2					
3		149.5	73.5	76.0	33.2	1.22
	2					
3		144.5	73.5	71.0	35.5	1.30
	2					
3		141.0	73.5	67.5	37.3	1.36
	2					
3		139.0	73.5	65.5	38.5	1.41
	2					
3		137.0	73.5	63.5	39.7	1.45

TABLE 11

PRESSURE-VOLUME DATA FOR CORE NOS. 4, 5 AND 7

Limestone

Core No.	4	5	7
Length	7.9 cm	8.03 cm	7.94 cm
Area	5.19 cm ²	5.19 cm ²	5.19 cm ²
Porosity	12.6%	12.6%	7.3%
Pore Volume	7.0 cc	6.8 cc	6.3 cc
Injection Rate (cc per hour)	400	400	400
Temperature	76°F	76°F	76°F

Test No.	Core No.	Pore Vol.		% SO ₂	P S I G			Permeability (md)	K/K _i
		Injected Water	SO ₂		Inlet	Outlet	Δ P		
8	4	7.5			109.8	79.8	30.0	83.4	1
			2	5					
		6			84.5	84.0	0.5	5000	60
9	5	20			208.0	78.0	130.0	19.5	1
			1	5					
		5			80.0	79.0	1.0	2500	128
10	7	20			204.0	74.0	130.0	19.3	1
			1	15					
		5			77.0	76.0	1.0	2500	130

TABLE 12

DISPLACEMENT TEST RECOVERY DATA - TEST NO. 12

Alundum Core No. RA 7918

Pore Volume = 60.0 cc

 $S_{wi} = 0.333$

Temperature = 150°F

Oil = Swan Hills Crude

Injected Phase = Distilled Water

Displacement Rate = 100 cc/hr

<u>Fluid Injected</u>		<u>Oil Produced</u>		<u>Water Produced</u>	<u>WOR</u>
<u>cc</u>	<u>% Pore Vol.</u>	<u>cc</u>	<u>% IOIP</u>	<u>cc</u>	
20.0	33.3	20.0	50.0		
26.0	43.3	26.0	65.0	0	WBT
27.0	45.0	26.2	65.5	0.8	4.0
29.0	48.4	26.4	66.0	1.6	4.0
32.0	53.3	27.1	67.8	4.9	4.7
34.0	56.6	27.4	68.5	6.6	5.7
38.0	63.4	27.7	69.3	10.3	12.3
42.0	70.0	27.8	69.5	14.2	39.0
46.0	76.6	27.9	69.7	18.1	39.0
51.0	85.0	28.0	70.0	23.0	49.0
59.0	98.4	28.2	70.5	30.8	49.0
64.0	106.8	28.5	71.3	35.5	15.7
69.0	115.0	28.6	71.5	40.4	49.0
74.0	123.3	28.7	71.8	45.3	49.0
84.0	140.0	28.9	72.3	55.1	49.0
90.0	150.0	29.0	72.5	65.0	58.0

TABLE 13

DISPLACEMENT TEST RECOVERY DATA - TEST NO. 13

Alundum Core No. RA 7918

Pore Volume = 60.0

 $S_{wi} = 0.333$

Temperature = 150°F

Oil = Swan Hills Crude

Injected Phase = 0.2% SO₂

Displacement Rate = 100 cc/hr

<u>Fluid Injected</u>		<u>Oil Produced</u>		<u>Water Produced</u>	<u>WOR</u>
<u>cc</u>	<u>% Pore Vol.</u>	<u>cc</u>	<u>% IOIP</u>	<u>cc</u>	
3.0	5.0	3.0	7.5	0	
25.8	43.0	25.8	64.5	0	WBT
27.1	45.1	26.1	65.3	1.0	3.3
28.5	47.5	26.5	66.3	2.0	2.5
31.1	51.8	27.1	67.8	4.0	3.3
33.3	55.5	27.3	68.3	6.0	10.0
35.5	59.2	27.5	68.8	8.0	10.0
37.6	62.6	27.6	69.0	10.0	20.0
39.6	66.6	27.7	69.3	12.0	20.0
41.8	69.7	27.8	69.5	14.0	20.0
44.9	74.8	27.9	69.8	17.0	30.0
48.0	80.0	28.0	70.0	20.0	30.0
49.8	83.0	28.1	70.3	21.7	-
54.9	91.5	28.2	70.5	26.7	33.0
60.3	100.5	28.6	71.5	31.7	12.5
70.8	118.0	29.1	72.8	41.7	20.0
74.8	124.7	29.1	72.8	45.7	-
90.0	150.0	29.6	74.0	60.4	37.0

TABLE 14DISPLACEMENT TEST RECOVERY DATA - TEST NO. 14

Alundum Core No. RA 7918

Pore Volume = 60.0 cc

 $S_{wi} = 0.333$

Temperature = 150°F

Oil = Swan Hills Crude

Injected Phase = 1% SO_2

Displacement Rate = 100 cc/hr

<u>Fluid Injected</u>		<u>Oil Produced</u>		<u>Water</u> <u>Produced</u>	<u>WOR</u>
<u>cc</u>	<u>% Pore Vol.</u>	<u>cc</u>	<u>% IOIP</u>	<u>cc</u>	
20.0	33.3	20.0	50.0		
26.0	43.4	26.0	65.0	0	WBT
27.5	45.9	26.3	65.7	1.2	4.0
28.5	47.5	26.5	66.3	2.0	4.0
31.0	51.6	27.0	67.5	4.0	4.0
33.3	55.5	27.3	68.3	6.0	6.7
35.6	59.4	27.6	69.0	8.0	6.7
37.8	63.0	27.8	69.5	10.0	10.0
41.0	68.4	28.0	70.0	13.0	15.0
45.0	75.0	28.1	70.3	17.0	40.0
48.5	80.9	28.2	70.5	20.3	33.0
53.7	89.5	28.4	71.0	25.3	25.0
59.0	98.4	28.7	71.8	30.3	16.7
64.3	107.2	29.0	72.3	35.3	16.7
69.5	116.0	29.2	73.0	40.3	25.0
73.5	122.5	29.3	73.3	44.3	40.0
90.0	150.0	29.6	74.0	60.4	53.7

TABLE 15

DISPLACEMENT TEST RECOVERY DATA - TEST NO. 15

Alundum Core No. RA 7918

Pore Volume = 60.0 cc

 $S_{wi} = 0.333$

Temperature = 150°F

Oil = Swan Hills Crude

Injected Phase = 5.0% SO₂

Displacement Rate = 100 cc/hr

<u>Fluid Injected</u>		<u>Oil Produced</u>		<u>Water</u>	<u>WOR</u>
<u>cc</u>	<u>% Pore Vol.</u>	<u>cc</u>	<u>% IOIP</u>	<u>Produced</u> <u>cc</u>	
20.0	33.3	20.0	50.0		
26.4	44.0	26.4	66.00	0	WBT
28.4	47.4	27.4	68.50	1.0	1.0
29.9	49.9	27.9	69.75	2.0	2.0
32.5	54.1	28.5	71.25	4.0	3.3
36.0	60.0	29.0	72.50	7.0	6.0
39.2	65.4	29.2	73.00	10.0	15.0
42.3	70.5	29.3	73.25	13.0	30.0
45.4	75.6	29.4	73.50	16.0	30.0
53.2	88.6	29.6	74.00	23.6	38.0
58.5	97.5	29.9	74.75	28.6	16.7
64.0	106.8	30.4	76.00	33.6	10.0
69.4	115.7	30.8	77.00	38.6	12.5
73.0	121.7	30.9	77.25	42.1	35.0
90.0	150.0	31.2	78.00	58.8	55.6

TABLE 16

DISPLACEMENT TEST RECOVERY DATA - TEST NO. 16

Alundum Core No. RA 7918

Pore Volume = 60.0 cc

 $S_{wi} = 0.333$

Temperature = 150°F

Oil = Swan Hills Crude

Injected Phase = 10% SO₂

Displacement Rate = 100 cc/hr

<u>Fluid Injected</u>		<u>Oil Produced</u>		<u>Water</u> <u>Produced</u>	<u>WOR</u>
<u>cc</u>	<u>% Pore Vol.</u>	<u>cc</u>	<u>% IOIP</u>	<u>cc</u>	
20.0	33.3	20.0	50.00		
27.0	40.0	27.0	67.50	0.0	WBT
28.3	47.2	27.3	68.25	1.0	3.3
30.6	51.0	27.6	69.00	3.0	6.7
33.0	55.0	28.0	70.00	5.0	5.0
35.2	58.6	28.2	70.50	7.0	10.0
37.4	62.4	28.4	71.00	9.0	10.0
40.7	67.9	28.7	71.75	12.0	10.0
44.0	73.4	29.0	72.50	15.0	10.0
47.3	78.9	29.3	73.25	18.0	10.0
51.8	86.4	29.7	74.25	22.5	11.0
55.5	92.5	30.0	75.00	25.5	10.0
58.8	98.0	30.3	75.75	28.5	10.0
62.0	103.4	30.5	76.25	31.5	15.0
65.1	108.5	30.6	76.50	34.5	30.0
68.3	114.0	30.8	77.00	37.5	15.0

TABLE 17

DISPLACEMENT TEST RECOVERY DATA - TEST NO. 17

Alundum Core No. RA 7918

Pore Volume = 60.0 cc

 $S_{wi} = 0.333$

Temperature = 150°F

Oil = Swan Hills Crude

Injected Phase = 15% SO₂

Displacement Rate = 100 cc/hr

<u>Fluid Injected</u>		<u>Oil Produced</u>		<u>Water</u> <u>Produced</u>	<u>WOR</u>
<u>cc</u>	<u>% Pore Vol.</u>	<u>cc</u>	<u>% IOIP</u>	<u>cc</u>	
27.5	45.8	27.5	68.70	0	WBT
29.9	49.8	27.9	69.80	2.0	5.00
32.5	54.1	28.5	71.20	4.0	3.33
34.9	58.1	28.9	72.30	6.0	5.00
37.2	62.0	29.2	73.00	8.0	6.67
39.5	65.9	29.5	73.80	10.0	6.67
43.0	71.6	30.0	75.00	13.0	6.00
46.5	77.5	30.5	76.30	16.0	6.00
54.0	90.0	31.1	77.70	22.9	11.50
57.5	95.9	31.6	79.00	25.9	6.00
60.5	101.0	31.6	79.00	28.9	-
63.6	106.0	31.7	79.25	31.9	30.0
67.7	113.0	31.8	79.50	35.9	40.0
70.7	118.0	31.8	79.50	38.9	-
73.5	122.5	31.8	79.50	41.7	-
90.0	150.0	31.8	79.50	58.2	-

TABLE 18

REACTION OF SULFUR DIOXIDE SOLUTIONS ON LIMESTONE CHIPS

% SO ₂	0.2	0.2	0.2	0.2	0.2	0.2	2	15	20
Pressure (psig)	0	340	1200	50	50	200	100	100	100
Temperature (°F)	75	75	75	72	200	250	75	75	70
Reaction Time (min.)	<u>pH</u>	<u>pH</u>	<u>pH</u>	<u>pH</u>	<u>pH</u>	<u>pH</u>	<u>pH</u>	<u>pH</u>	<u>pH</u>
0	1.85	1.85	1.85	1.85	1.85	1.85	1.20	0.88	0.80
2	2.75	2.80	3.05	2.75	3.00	3.35	1.80	1.80	1.55
4	3.10	3.31	3.67	3.10	3.30	3.45	2.20	2.00	1.65
6	3.62	3.80	4.20	3.60	3.77	3.82	2.40	2.20	1.68
8	4.10	4.30	4.50	4.10	4.02	4.50	2.50	2.30	1.68
10	4.33	4.58	4.60	4.35	4.40	5.05	2.75	2.40	1.68
15	4.65	4.80	4.80	4.65	4.95	5.20	2.95	2.45	1.68
20	4.80	4.91	4.90	4.80	5.25	5.50	3.05	2.50	1.70
30							3.15	2.58	1.75
60							3.40	2.58	

TABLE 19

pH VERSUS PERCENT SULFUR DIOXIDE

Temperature 68°F

<u>% SO₂</u>	<u>pH</u>	<u>% SO₂</u>	<u>pH</u>
0.005	3.19	0.15	1.90
0.01	2.90	0.20	1.85
0.03	2.51	1.38	1.30
0.05	2.33	2.00	1.20
0.10	2.10	15.00	0.88
		20.00	0.80

TABLE 20RADIAL FLOW TESTS OBSERVING CHANGE IN PERMEABILITY

Core No. 10

Test No. 20 - .04% SO₂

Pore Volume = 63.5 cc

Outside Diameter = 11.049 cm

Temperature = 70°F

Length = 9.576 cm

Pore Vol. Injected	P S I G			Time (sec.)		Q/ Δ P (cc/sec-atm)	K/K _i
	Inlet	Outlet	Δ P	Total	Δ T		
0	213.0	83.0	130.0			.0102	1.000
1	223.0	83.0	140.0	592	592	.0114	1.120
2	222.0	83.0	139.0	1150	558	.0121	1.185
3	222.0	83.0	139.0	1686	536	.0126	1.235
4	223.0	84.0	139.0	2218	532	.0127	1.245
5	223.0	85.0	138.0	2736	518	.0136	1.330
6	223.0	83.0	140.0	3243	507	.0133	1.300
6.3	223.0	83.0	140.0	3395	152	.0132	1.290

TABLE 21RADIAL FLOW TESTS OBSERVING CHANGE IN PERMEABILITY

Core No. 10

Test No. 21 - .04% SO₂

Pore Volume = 63.5 cc

Outside Diameter = 11.049 cm

Temperature = 70°F

Length = 9.576 cm

<u>Pore Vol.</u> <u>Injected</u>	<u>P S I G</u>			<u>Time (sec.)</u>		<u>Q/ΔP</u> <u>(cc/sec-atm)</u>	<u>K/K_i</u>
	<u>Inlet</u>	<u>Outlet</u>	<u>ΔP</u>	<u>Total</u>	<u>ΔT</u>		
0	228.0	85.0	143.0			.0126	1.000
1	228.0	85.0	143.0	521	521	.0126	1.000
2	227.0	85.0	142.0	1036	515	.0128	1.016
3	227.0	85.0	142.0	1530	494	.0134	1.063
4	228.0	86.0	142.0	2025	495	.0134	1.063
5	228.0	86.0	142.0	2503	478	.0138	1.095
6	228.0	86.0	142.0	2982	479	.0138	1.095
6.3	228.0	86.0	142.0	3123	141	.0141	1.120

TABLE 22

RADIAL FLOW TESTS OBSERVING CHANGE IN PERMEABILITY

Core No. 10

Test No. 22 - .04% SO₂

Pore Volume = 63.5 cc

Outside Diameter = 11.049 cm

Temperature = 70°F

Length = 9.576 cm

Pore Vol. Injected	P S I G			Time (sec.)		Q/ Δ P (cc/sec-atm)	K/K _i
	Inlet	Outlet	Δ P	Total	Δ T		
0	257.5	86.0	171.5			.0148	1.000
1	257.0	86.0	171.0	352	352	.0154	1.040
2	257.0	86.0	171.0	706	354	.0156	1.050
3	257.0	86.0	171.0	1047	337	.0163	1.100
4	256.5	86.0	170.5	1386	339	.0163	1.100
5	256.5	86.0	170.5	1714	328	.0168	1.140
6	256.5	86.0	170.5	2046	332	.0166	1.120
6.3	256.5	86.0	170.5	2155	109	.0169	1.140

TABLE 23RADIAL FLOW TESTS OBSERVING CHANGE IN PERMEABILITY

Core No. 10

Test No. 23 - .20% SO₂

Pore Volume = 63.5 cc

Outside Diameter = 11.049 cm

Temperature = 70°F

Length = 9.576 cm

Pore Vol. Injected	P S I G			Time (sec.)		Q/ Δ P (cc/sec-atm)	K/K _i
	Inlet	Outlet	Δ P	Total	Δ T		
0	263.5	87.5	176.0			.0169	1.00
1	262.5	87.5	175.0	306	306	.0175	1.035
2	262.0	87.5	174.5	605	299	.0180	1.065
3	262.0	87.5	174.5	874	269	.0205	1.19
4	261.0	87.5	173.5	1128	254	.0213	1.26
5	260.0	87.5	172.5	1324	196	.0278	1.65
6	259.0	88.0	171.0	1481	157	.0350	2.07
6.3	258.5	88.0	170.5	1521	40	.0422	2.50

TABLE 24RADIAL FLOW TESTS OBSERVING CHANGE IN PERMEABILITY

Core No. 10

Test No. 24 - .20% SO₂

Pore Volume = 63.5 cc

Outside Diameter = 11.049 cm

Temperature = 70°F

Length = 9.576 cm

<u>Pore Vol.</u> <u>Injected</u>	<u>P S I G</u>			<u>Time (sec.)</u>		<u>Q/ΔP</u> <u>(cc/sec-atm)</u>	<u>K/K_i</u>
	<u>Inlet</u>	<u>Outlet</u>	<u>ΔP</u>	<u>Total</u>	<u>ΔT</u>		
0	206.0	91.0	115.0			.0338	1.00
1	205.5	91.0	114.5	182	182	.0450	1.33
2	205.0	92.5	112.5	313	131	.0638	1.89
3	205.0	93.0	112.0	410	97	.0860	2.54
4	204.5	93.5	111.0	492	82	.1025	3.03
5	204.5	94.0	110.5	563	71	.1200	3.55
6	204.0	94.0	110.0	629	66	.1295	3.83
6.3	204.0	94.0	110.0	648	19	.1350	4.00

TABLE 25RADIAL FLOW TESTS OBSERVING CHANGE IN PERMEABILITY

Core No. 10

Test No. 25 - .20% SO₂

Pore Volume = 63.5 cc

Outside Diameter = 11.049 cm

Temperature = 70°F

Length = 9.576 cm

<u>Pore Vol.</u> <u>Injected</u>	<u>P S I G</u>			<u>Time (sec.)</u>		<u>Q/ΔP</u> <u>(cc/sec-atm)</u>	<u>K/K_i</u>
	<u>Inlet</u>	<u>Outlet</u>	<u>ΔP</u>	<u>Total</u>	<u>ΔT</u>		
0	118.0	90.0	28.0			.134	1.00
1	117.0	90.5	26.5	226	226	.157	1.17
2	116.0	91.0	25.0	401	175	.215	1.60
3	116.0	91.0	25.0	555	154	.244	1.82
4	116.0	92.0	24.0	690	135	.290	2.16
5	116.0	92.0	24.0	816	126	.311	2.32
6	116.0	92.0	24.0	933	117	.335	2.50
6.3	116.0	92.0	24.0	968	35	.345	2.57

SAMPLE CALCULATIONSCHANGE IN PERMEABILITYPore Volume

Core No. 6

$$\text{Bulk Volume} = 7.94 \times \frac{2.57^2}{4} \pi = 41.21 \text{ cc}$$

$$\text{Pore Volume} = 41.21 \times 0.173 = 7.129 \text{ cc}$$

Permeability

Linear Core No. 6

$$K_i = \frac{Q \mu L}{A \Delta P} = \frac{400}{3600} \times \frac{1}{1} \times \frac{7.94}{1} \times \frac{1}{5.19} \times \frac{14.7}{27.5} = 91.0 \text{ md}$$

Where: $Q = 400/3600$ cc per sec. $\mu = 1.0$ cp (water - 20°C) $L = 7.94$ cm $A = 5.19$ cm² $P = 27.5/14.7$ atm.

Radial Core No. 10

$$K_i = \frac{Q \mu \ln \frac{r_e}{r_w}}{2 \pi h (P_e - P_w)} = \frac{0.077 \times 1.03 \times \ln \frac{11.049}{1.303} \times 14.7}{2 \pi \times 9.576 (195.5 - 84.0)}$$

$$= 0.000356 \text{ darcy}$$

$$= 0.356 \text{ md.}$$

Where: $Q = 0.077$ cc per sec. $\mu = 1.03$ cp. (water - 19°C) $r_e =$ outside diameter of core 11.049 cm $r_w =$ inside diameter of core 1.303 cm $h =$ height of core 9.576 cm $P_e =$ Pressure at outside diameter 195.5/14.7 atm $P_w =$ Pressure at inside diameter 84.0/14.7 atm

$$\frac{Q}{\Delta P} = \frac{0.077}{1} \times \frac{14.7}{195.5-84.0} = 0.0102 \frac{\text{cc}}{\text{sec-atm}}$$

SAMPLE CALCULATIONS (Continued)DISPLACEMENT TESTS

Volume of oil in place

Core No. RA 7918

$$\text{Pore Volume} = 45.5 \times \frac{2.54^2}{4} \pi \times 0.26 = 60.0 \text{ cc}$$

$$\begin{aligned}\text{IOIP} &= 60.0 \times (1 - S_{wi}) \\ &= 60.0 \times (1 - 0.333) \\ &= 40.0 \text{ cc}\end{aligned}$$

CORE DESCRIPTION

<u>Core Description</u>	<u>Number</u>	<u>Length (cm)</u>	<u>Diameter (cm)</u>	<u>Porosity %</u>
Linear	4-L	7.83	2.54	8.3
Limestone	4	7.90	2.57	12.6
	5	8.03	2.57	12.6
	6	7.95	2.57	17.3
	7	7.94	2.57	7.3
	13	7.98	2.57	13.7
	14	7.93	2.57	11.2
	16	8.00	2.57	15.2
Radial Limestone	10	9.576	11.049	6.7
Alundum	RA 7918	45.5	2.54	26.0
	TA 7919	45.5	2.54	24.2

B29875